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1915.

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		0 = 16.			0 = 16
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	Sb	120·2	Neodymium	Nd	144·3
	A	39·88	Neon	Ne	20·2
	As	74·96	Nickel	Ni	58·68
	Ba	157·37	Niton (radium emanation)	Nt	222·4
	Bi	208·0	Nitrogen	N	14·01
	B	11·0	Osmium	Os	190·9
	Br	79·92	Oxygen	O	16·00
	Cd	112·40	Palladium	Pd	106·7
	Cs	132·81	Phosphorus	P	31·04
	Ca	40·07	Platinum	Pt	195·2
	C	12·00	Potassium	K	39·10
	Ce	140·25	Praseodymium	Pr	140·6
	Cl	35·46	Radium	Ra	226·4
	Cr	52·0	Rhodium	Rh	102·9
	Co	58·97	Rubidium	Rb	85·45
	Cb	93·5	Ruthenium	Ru	101·7
	Cu	63·57	Samarium	Sa	150·4
	Dy	162·5	Scandium	Sc	44·1
	Er	167·7	Selenium	Se	79·2
	Eu	152·0	Silicon	Si	28·3
	F	19·0	Silver	Ag	107·88
	Gd	157·3	Sodium	Na	23·00
	Ga	69·9	Strontium	Sr	87·63
	Ge	72·5	Sulphur	S	32·07
	Gl	9·1	Tantalum	Ta	181·5
	Au	197·2	Tellurium	Te	127·5
	He	3·99	Terbium	Tb	159·2
	Ho	163·5	Thallium	Tl	204·0
	H	1·008	Thorium	Th	232·4
	In	114·8	Thulium	Tm	168·5
	I	126·92	Tin	Sn	119·0
	Ir	193·1	Titanium	Ti	48·1
	Fe	55·84	Tungsten	W	184·0
	Kr	82·92	Uranium	U	238·5
	La	139·0	Vanadium	V	51·0
	Pb	207·10	Xenon	Xe	130·2
	Li	6·94	Ytterbium (Neoytterbium)	Yb	172·0
	Lu	174·0	Yttrium	Yt	89·0
	Mg	24·32	Zinc	Zn	65·37
	Mn	54·93	Zirconium	Zr	90·6
	Hg	200·6			

CCXL.—*Catalysis. Part XVIII.*   *The Reactions Both the Ions and the Molecules of Acids, Bases and Salts: The Reactions of Alkyl Haloids with Phenoxides and Ethoxides.*

By John Hanston Shroder and Solomon Farley Acree.

The two recent papers by Segaller (T., 1913, **103**, 1154, 1421) the action of alkyl haloids on sodium phenoxide show that reaction-velocity increases with dilution, the formula

$$K_v = K_1 + a \log V,$$

used by Hecht, Conrad, and Brückner (*Zeitsch. physikal. Chem.*, 1890, **5**, 289), applying equally well to Segaller's results. Since the brilliant work of Arrhenius on the ionic theory, and Ostwald on the relation between the ionisation of acids and activity in ester catalysis, inversion of sucrose and hydrolysis acetamide, chemists generally, Kahlenberg (*J. Physical Chem.*, 1901, **5**, 339; 1902, **6**, 1) especially, Michael (*Amer. Chem. J.*, 1910, **43**, 322) and Armstrong being notable exceptions, believed that only ions enter appreciably into chemical reactions. Even the known "deviations from the ionic reaction," especially those produced by added salts, were thought to be due to a change in the ionic reaction by the salts themselves. As was pure chance that Arrhenius and Ostwald worked with reactions in which ions are chiefly concerned, and as the "deviations from the ionic reaction" or "salt catalysis" observed by them may be partly or wholly due to the reactions of the non-ionised electrolytes, the workers in this laboratory have since 1905 developed the theory that both the ions and molecules of acids, bases, and salts, must in all cases be examined for activity. Johnson and Acree in 1907 (*Amer. Chem. J.*, **37**, 410; **38**, 258) brought out this idea clearly for salts, and in 1908 Shadinger and Acree said "We are studying the problem whether acids, bases and salts enter into these reactions through their ions or molecules, or both." Besides the discussion of "salt catalysis" (*ibid.*, 1908, **39**, 228) we gave the equation (*ibid.*, p. 228) $dx/dt = K_{\text{ions}} a(1 - x)$ for the reactions of the ions, as Arrhenius, Ostwald, and all others of them have done, and then gave (*ibid.*, p. 228) the equation $dx/dt = K'_{\text{ions}}(1 - a)(1 - x)^2$ for the activity of the "unionised acid, base or salt," this idea and equation being the first contribution to the theory of chemical reactions and the activity
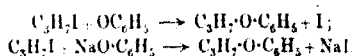
the deviations from the ionic reactions" or "salt catalysis" since Arrhenius' brilliant work in 1885. Before the American Chemical Society in Baltimore, in December, 1908 (*Science*, **30**, 624), one of us stated that: "We see, then, that the question whether the ions or *cation* (simple or complex) or the *molecular form* of a given acid, base, salt or other neutral substance, is the chief constituent transformed directly into the end products depends entirely upon the relative magnitudes of the various constants, and therefore varies widely in the different problems." Our work (*Amer. Chem. J.*, 1912, **48**, 352; 1913, **49**, 116, 127, 345, 369, 474, and earlier papers) has now shown that this new idea of the activity of non-ionised electrolytes is fully as important for chemical reactions as the idea that ions are active. To express reaction velocities completely, we must use the equation

$$K_N = \{K_i a + K_m(1 - a)\}[1 - (f)C_{cat}].$$

The second term on the right side of the equation represents a factor for "salt catalysis," and the first term gives the activity of the ions and molecules in normal solutions having the ionisation a and the velocity K_N. This theory has been found to hold in about thirty reactions studied by us in concentrated solutions (N to $N/32$), as well as in ideal solutions ($N/32$ to $N/2048$), the reactions involving the three most important classes of chemical changes, namely, metathesis, pure catalysis and intramolecular rearrangement. By this theory we have been able to reinterpret the later work of Arrhenius, Ostwald, Conrad and his co-workers, Lapworth, Tubandt, Stieglitz, Bredig, Goldschmidt, Holmberg, Biddle, Walker, van Dam, Blanksma and Segaller as reactions of molecules and molecules, instead of ions alone. The theory has, furthermore, now been accepted and used by Arrhenius (Taylor and Arrhenius, *Medd. K. Vetenskapsakad. Nobelinst.*, 1913, **2**, Nos. 34, 35, 37), Stieglitz (*J. Amer. Chem. Soc.*, 1912, **34**, 1687, 1689, 1690, 1694; 1913, **35**, 1774), Dawson (T., 1913, **103**, this vol., p. 1093), Goldschmidt (*Zeitsch. Elektrochem.*, 1909, and *Zeitsch. physikal. Chem.*, 1910, **70**, 627), Bredig (*Zeitsch. physikal. Chem.*, 1912, **18**, 535, 543; *Zeitsch. physikal. Chem.*, 1913, **85**, 129, 170, 211), Holmberg (*Zeitsch. physikal. Chem.*, 1913, **84**, 451, 468, 469), Biddle (*J. Amer. Chem. Soc.*, 1914, **36**, and earlier papers), Kilpi (*Zeitsch. physikal. Chem.*, 1913, **86**, 430, and Worley (*Phil. Mag.*, 1914, [vi], **27**, 459), and bids fair to become generally useful in all reactions involving electrolytes.

Segaller studied the reactions of $N/2$-sodium phenoxide with a number of different alkyl haloids at $42.5°$ in order to measure their relative chemical activities. Fortunately, he investigated the

action of n-propyl iodide on varying concentrations of sodium phenoxide, and it is this work that interests us at present and extends our series of investigations with methyl and ethyl iodides at 25° and 35°. Lack of time alone is all that has prevented us from using all the other alkyl haloids in our work on the oxides, ethoxides, and urazoles. We have now extended Segaller's data to obtain the reaction-velocities for solutions $N/2$, $N/4$, $N/10$, and $N/20$, and have found by the use of the equation, $K_N = K_i a + K_m(1-a)$, that his data harmonise completely with ours and with our theory, both the phenoxide ions and the non-ionised sodium phenoxide seeming to react with propyl iodide, as follows

$$C_3H_7I + OC_6H_5 \longrightarrow C_3H_7 \cdot O \cdot C_6H_5 + I;$$
$$C_3H_7I + NaO \cdot C_6H_5 \longrightarrow C_3H_7 \cdot O \cdot C_6H_5 + NaI.$$

The following tables show the values of K_i and K_m obtained by us from our own work on methyl and ethyl iodides and sodium potassium, and lithium phenoxides at 25° and 35°, and the Segaller's work at 42·5°. Because of larger experimental error the values of K_i do not agree as well at 35° as at 25°. The values of a used by us in recalculating Segaller's data were obtained by extrapolation of H. C. Robertson's data for sodium phenoxide at 0°, 25°, and 35°. It is seen that the ratio K_i/K_m for both methyl iodide and ethyl iodide and sodium phenoxide is from 5 to 6 at 25°, and 6 to 7 at 35°, whilst for propyl iodide it is about 17 at 25°, and the reaction is almost purely ionic in solutions more dilute than N/50. The value for K_i for the phenoxide ion and ethyl iodide is about five times as large at 25° and 35° as that for ethyl iodide, which in turn is about three times the value of K_i found for the phenoxide ion and propyl iodide at 42·5°.

Temperature, 25°.

	K_i	K_m
Sodium phenoxide and methyl iodide ...	0·0282	0·00477
Potassium ,, ,, ,, ,, ...	0·0283	0·00507
Lithium ,, ,, ,, ,, ...	0·0287	0·00507
Sodium phenoxide and ethyl iodide ...	0·00551	0·000827
Potassium ,, ,, ,, ,, ...	0·00518	0·000929
Lithium ,, ,, ,, ,, ...	0·00534	0·000870

Temperature, 35°.

Sodium phenoxide and methyl iodide ...	0·0909	0·0137
Potassium ,, ,, ,, ,, ...	0·1036	0·01658
Sodium phenoxide and ethyl iodide ...	0·0183	0·00347
Potassium ,, ,, ,, ,, ...	0·0197	0·00347
Lithium ,, ,, ,, ,, ...	0·0174	0·00347

Temperature, 42·5°.

| Sodium phenoxide and propyl iodide ... | 0·0128 | 0·00073 |

Our chief interest in Segaller's work and that of Hecht, Conrad, and Brückner lies in the fact that the change in K_N with dilution follows the equation $K_N = K_1 + a \log V$, as written by Hecht, Conrad, and Brückner. A more general form is

$$K'_N - K_N = a \log (V'/V),$$

in which K'_N and K_N represent $1/K_N$ and $1/K_N$, the reaction-velocities for the concentrations $1/V'$ and $1/V$, as used in our former papers. This equation is purely empirical, has never been on any scientific foundation, and it does not involve the changing ionisation of the ethoxide or phenoxide, because Hecht, Conrad, and Brückner did not consider the possibility of the ionisation of the sodium ethoxide or phenoxide, but spoke of all these substances as non-electrolytes, or "nichtleitende Körper." We have therefore interested ourselves in determining why this simple equation holds so excellently, as it undoubtedly does, for the work of Hecht, Conrad, and Brückner, Segaller, and for a part of ours to which we have applied it.

When we write Conrad's equation as (1) $K'_N - K_N = a \log (V'/V)$, and one of our simultaneous equations as (2) $K_N = K_i a + K_m (1 - a)$ and (3) $K'_N = K_i a' + K_m (1 - a')$, and subtract (2) from (3), we get $K'_N - K_N = (K_i - K_m)(a' - a)$. By comparing equations (2) and we get (5) $K'_N - K_N = a \log (V'/V) = (K_i - K_m)(a' - a)$, and this (6) $a = \dfrac{(K_i - K_m)(a' - a)}{\log (V'/V)}$ and (7) $a = \dfrac{K'_N - K_N}{\log (V'/V)}$. The $\log (V'/V)$ of Conrad's equation (1) has a scientific basis, therefore, only if equation (6) actually gives "constants" for a. We have recalculated Segaller's work, and Dr. W. A. Taylor has that of Hecht, Conrad, and Brückner, and we have also applied these equations to much of our own work; we find that equations (6) and (7) hold excellently within the experimental errors. Of course the central point hinges on the validity of the relation

$\dfrac{a}{V} = K$, an empirical equation that holds very well in the

concentrated solutions of a number of electrolytes to which we have applied it, whether the electrolyte obeys the Ostwald dilution law or is too "strong" to do so. This equation cannot hold for all concentrations, because the ratio V'/V keeps on increasing after complete ionisation is reached, whereas $a' - a$ then becomes constant. We are investigating all these relations fully, and extended reports on the work of Segaller, and of Hecht, Conrad, and Brückner, will soon be published by Dr. J. H. Shroder and W. A. Taylor.

As seen in tables VI of both sections of the experimental portion that both equations (6) and (7) give very good constants for

a, the two values, 0·00265 and 0·00269, for sodium phenxxx... propyl iodide at 42·5° agreeing better than the values 0·xx·x... 0·02594 for sodium ethoxide and methyl iodide at 24°. It ... x... in tables VII of both sections that the values for "K_N cxx·x... agree well with those for "K_N found."

It is thus seen that the empirical relation

$$K'_N - K_N = a \log (V'/V)$$

used by Hecht, Conrad, and Brückner, and by Segaller, xx... relation $K'_N = K_N$ observed by Bredig (*Zeitsch. Elektrochxx... *10**, 582), Tubandt (*Annalen*, 1905, **339**, 41; 1907, 354 ... 1910, **377**, 284), Steger (*Rec. trav. chim.*, 1899, **18**, 13, 4... by McCombie and Scarborough (this vol., p. 1304), and Myxx... Acree (*Amer. Chem. J.*, 1912, **48**, 358; 1913, **49**, 141, x·7·... the salt catalysis equation, $K_N = K_i a + K_a a^2$, or its equivxxx... by Arrhenius, Spohr, Euler, Stieglitz and others, are all sxx... cases that can be converted into our general equation

$$K_N = [K_i a + K_m(1 - a)][1 + (f)C_{xxx}],$$

involving the reactions of both the ions and the non-ionxxx... of acids, bases, and salts.

Interaction of Sodium Phenoxide and Propyl Iodide at 4.

TABLE I.

K_N *Found for Sodium Phenoxide and Propyl Iodide at 4.*

Concentration of sodium phenoxide. V.	K_N.	K_N average.	Concentration of sodium phenoxide. V.	K_N. k ...
2	0·00280		10	0·00180
	0·00293			0·00475 x·x·x
	0·00305		20	0·00552
	0·00309	0·00297		0·00571 x·x·x
4	0·00369			
	0·00371	0·00370		

TABLE II.

Ionisation of Sodium Phenoxide at 42·5°.

V.	a.	$1-a$.
2	0·1826	0·8174
4	0·2400	0·7600
10	0·3265	0·6735
20	0·4065	0·5935

TABLE III.

K_i and K_m *Found for Sodium Phenoxide and Propyl Iodide at* $42.5°$.

	K_i	K_m
$V = 2 : V = 4$	0.01337	0.000648
$V = 2 : V = 10$	0.01325	0.000673
$V = 2 : V = 20$	0.01264	0.000809
$V = 4 : V = 10$	0.01319	0.000704
$V = 4 : V = 20$	0.01246	0.000832
$V = 10 : V = 20$	0.01185	0.001364*
Average	0.01280	0.000753

* This value was omitted.

TABLE IV.

K_i *Calculated and Found for Sodium Phenoxide and Propyl Iodide at* $42.5°$.

V.	K_i.	K, calculated.	Error, per cent.
2	0.00297	0.00295	- 0.7
4	0.00370	0.00364	- 1.6
10	0.00478	0.00469	- 1.9
20	0.00562	0.00565	0.5

TABLE V.

Per Cent. of Reaction Due to Ions and to Molecules.

Titration of sodium phenoxide V.	Per cent. of reaction due to $a K_i$.	Per cent. of reaction due to $(1-a)K_m$.
2	79.14	20.86
4	84.40	15.60
10	89.10	10.90
20	92.09	7.91

TABLE VI.

a *Found for Sodium Phenoxide and Propyl Iodide at* $42.5°$.

	$a = \dfrac{K_i - K_s}{\log(V/V)}$	$a = \dfrac{(K - K_m)(a - a)}{\log(V/V)}$
$V = 2 : V = 4$	0.002425	0.002297
$V = 2 : V = 10$	0.002589	0.002480
$V = 2 : V = 20$	0.002650	0.002698
$V = 4 : V = 10$	0.002713	0.002618
$V = 4 : V = 20$	0.002746	0.002870
$V = 10 : V = 20$	0.002780	0.003205
Average	0.00265	0.00269

TABLE VII.

K_x *Found*, K_N *Calculated [obtained by using* "a" *in the* F... $K'_N = K_N + a \log (V'/V)$], *and Percentage Error*

V.	K_x found.	K, calculated. for $a = 0.00265$.	Error in per cent.	K, calculated. for $a = 0.00269$.	...
2	0.00297	0.002970	0.00	0.00297	...
4	0.00379	0.003767	−1.77	0.00378	...
10	0.00478	0.004820	0.83	0.00485	...
20	0.00562	0.005620	0.00	0.00566	...

Interaction of Sodium Ethoxide and Methyl Iodide ...

TABLE I.

K_N *Found for Sodium Ethoxide and Methyl Iodide* ...

Concentration of sodium ethoxide	K..	Concentration of sodium ethoxide	K ...
1	0.05512	20	0.0808.
2	0.06276	40	0.0948.
5	0.07182	80	0.1022
10	0.07950		

TABLE II.

Ionisation of Sodium Ethoxide at 24°.

V.	a.	1 − a.	V.	a.	1 − a
1	0.1470	0.8530	20	0.5075	0.492.
2	0.2346	0.7654	40	0.6040	0.396.
5	0.3335	0.6665	80	0.7030	0.297
10	0.4170	0.5830			

TABLE III.

K_i *and* K_m *Found for Sodium Ethoxide and Methyl Iodide* ...

V.			K..	K ..
V.	1 : V	2	0.1294	0.04230
V.	1 : V	5	0.1215	0.04191
V.	1 : V	10	0.1312	0.04184
V.	1 : V	20	0.1304	0.04212
V.	1 : V	40	0.1284	0.04241
V.	1 : V	80	0.1274	0.04264
V.	2 : V	5	0.1328	0.04126
V.	2 : V	10	0.1330	0.04112.
V.	2 : V	20	0.1306	0.04194
V.	2 : V	40	0.1281	0.04260
V.	2 : V	80	0.1273	0.04290.
V.	5 : V	10	0.1331	0.04114
V.	5 : V	20	0.1297	0.04280
V.	5 : V	40	0.1276	0.04380
V.	5 : V	80	0.1267	0.04433
V.	10 : V	20	0.1275	0.04540
V.	10 : V	40	0.1262	0.04608
V.	10 : V	80	0.1258	0.04630
V.	20 : V	40	0.1253	0.04740
V.	20 : V	80	0.1255	0.04720
V.	40 : V	80	0.1256	0.04700
		Average	0.1287	0.04354

TABLE IV.

K_s *Calculated and Found for Sodium Ethoxide and Methyl Iodide at* 24°.

K_s	K_s calculated.	Error in per cent.	V	K_s	K_s calculated.	Error in per cent.
0.05512	0.05605	- 1.68	20	0.08696	0.08676	- 0.23
0.06276	0.06352	- 1.21	40	0.09448	0.09498	0.52
0.07182	0.07194	- 0.16	80	0.1022	0.1034	1.17
0.07950	0.07905	+ 0.57				

TABLE V.

Per Cent. of Reaction Due to Ions and to Molecules.

Concentration of ethoxide.	Per cent. of reaction due to aK_s	Per cent. of reaction due to $(1-a)K_m$	Concentration of sodium ethoxide.	Per cent. of reaction due to aK_s	Per cent. of reaction due to $(1-a)K_m$
1	33.75	66.25	20	75.28	24.72
2	47.53	52.47	40	81.84	18.16
5	59.66	40.34	80	87.51	12.49
10	67.89	32.11			

TABLE VI.

c *Found for Sodium Ethoxide and Methyl Iodide at* 24°.

	a	$\dfrac{K_s - K_m}{\log(V_1/V)}$	a	$\dfrac{(K_s - K_m)(a - a)}{\log(V_1/V)}$
V	1 : $V = 2$	0.02538		0.02478
V	1 : $V = 5$	0.02588		0.02571
V	1 : $V = 10$	0.02438		0.02299
V	1 : $V = 20$	0.02447		0.02359
V	1 : $V = 40$	0.02456		0.02851
V	1 : $V = 80$	0.02474		0.02921
V	2 : $V = 5$	0.02276		0.02116
V	2 : $V = 10$	0.02393		0.02221
V	2 : $V = 20$	0.02420		0.02720
V	2 : $V = 40$	0.02438		0.02837
V	2 : $V = 80$	0.02431		0.02923
V	5 : $V = 10$	0.02551		0.02328
V	5 : $V = 20$	0.02515		0.02461
V	5 : $V = 40$	0.02509		0.02550
V	5 : $V = 80$	0.04523		0.02622
V	10 : $V = 20$	0.02478		0.02560
V	10 : $V = 40$	0.02488		0.02944
V	10 : $V = 80$	0.02513		0.02697
V	20 : $V = 40$	0.02498		0.02730
V	20 : $V = 80$	0.02531		0.02768
V	40 : $V = 80$	0.02564		0.02800
	Average	0.02470		0.02594

TABLE VII.

K_N *Found,* K_N *Calculated* {*obtained by using* "a" *in the* $E_{\text{c...}}$
$K'_N = K_N + a \log (V'/V)$}, *and Percentage Error.*

V.	K_N found.	K, calculated for $a = 0.02470$.	Error, per cent.	K, calculated for $a = 0.02394$.	E...
1	0.05512	0.05458	−0.99	0.05372	...
2	0.06276	0.06199	+1.24	0.06150	...
5	0.07182	0.07182	−0.00	0.07182	...
10	0.07950	0.07948	+0.03	0.07963	...
20	0.08696	0.08669	−0.31	0.08743	...
40	0.09448	0.09412	−0.36	0.09524	...
80	0.10220	0.10159	−0.59	0.10305	...

Conclusions.

(1) It has been shown that the work of Hecht, Con... Brückner on the interaction of methyl iodide and sodium et... at $24°$, and that of Segaller on the interaction of n-prop... and sodium phenoxide at $42.5°$, harmonises with our ... along these lines. Their data give constants for K_i and K_m... substituted in the equation $K_N = K_i a + K_m(1 - a)$, and ... excellent evidence that both the ethoxide and phenoxide ... well as the non-ionised sodium ethoxide and sodium phen... molecules, react with the alkyl haloids. The values K_i ... and K_m 0.04354 are found for methyl iodide and sodium et... at $24°$, whereas $K_i = 0.0128$ and $K_m = 0.000753$ are foun... sodium phenoxide and propyl iodide at $42.5°$.

(2) Hecht, Conrad, and Brückner, and Segaller, found th... reaction-velocities can be expressed accurately by the eq... $K'_N = K_N + a \log (V'/V)$, an equation which does not take into... sideration the changing values of the ionisation of the eth... and phenoxides. We have found that this equation har... with our theory and the equation $K_N = K_i a + K_m(1 - a)$, in... of the fact that the changes in volume, ionisation, and rea... velocity correspond closely with the equations

$$a = \frac{K'_N - K_N}{\log (V'/V)} = \frac{(K_i - K_m)(a' - a)}{\log (V'/V)}.$$

We are indebted to the Carnegie Institution of Washing... aid in this work.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD.

CCXLI.—*The Limits of Inflammability of Mixtures of Methane and Air.*

By MAURICE JOHN BURGESS and RICHARD VERNON WHEELER.

IN a recent communication (this vol., p. 1859) Coward and Brinsley suggested that "inflammability must be regarded as a specific property, either present or absent, of any given gaseous mixture under definite conditions of temperature and pressure" (p. 1884); independent of the shape and size of the vessel containing it, and dependent also of the nature of the means used for ignition in the first place" (p. 1861).

On the basis of this definition, a "criterion" of inflammability was put forward, which, stated briefly, demands that the true "limit mixture" must be regarded as that in which flame can be propagated upwards—indefinitely.

It is well known that mixtures of methane, for example, and air have different limits of inflammability, both higher and lower, dependent on the direction in which the flame has to travel.[*] Coward and Brinsley were probably led to their choice as to what constitutes a true "limit-mixture" by consideration of the fact that a smaller percentage of inflammable gas is required (they say only with the lower-limit) for upward than for downward propagation of flame, and by the belief that the experimental conditions specified by them disclosed the least quantities of the combustible gases, hydrogen, methane, and carbon monoxide, that are capable of forming with air mixtures in which self-propagation of flame can take place.

It does not seem to us desirable so to restrict the use of the term "limit mixture." The most important industry in which knowledge of the limits of inflammability of gaseous mixtures is required is coal-mining. The occurrence of fire-damp in mines constitutes, as is well known, one of the gravest dangers to the industry; not so much, it is believed, because of the possibility of widespread explosions taking place in fire-damp and air mixtures extending through the workings, modern legislation regarding the ventilation of mines having rendered such occurrences exceedingly unlikely, but because a local accumulation of fire-damp, forming an explosive mixture with the air, may become ignited and transmit flame to

[*] This fact has been emphasised by Professor Enrique Hauser in a brochure entitled "Leçons sur le grisou" (Madrid, 1908). Hauser has summarised the best results given by various experimenters for the limits of inflammability of these air mixtures, and has offered an explanation of the differences.

any fine coal dust that may be deposited on the roadways ...
produce a widespread coal-dust explosion.

Legislation has attempted to deal also with this dang...
stipulating that frequent analyses shall be made of the air ...
mine roadways and workings, and precautions taken to pr...
the percentage of methane contained in the air from exce...
certain minimum. Despite precautions, accumulations of fire...
usually near the roof, sometimes occur; and, should suffi...
damp mingle with the ventilating current and by some m...
encounter a sufficiently intense source of heat, what is te...
called a "local ignition" may occur. In the majority of ...
no damage or loss of life is caused by these "local ign...
which usually take the form of a slowly-moving flame ...
roof.

Such cases of the propagation of flame in fire-damp air m...
are those most frequently reported. It will be realised th...
danger lies in the existence, over a considerable length of r...
of a mixture in which a flame can travel horizontally. A s...
danger arises when, as has been known to happen, a fall of...
of the roof liberates, and distributes in the ventilating cur...
quantity of fire-damp that has accumulated in cavities ab...
roof.

A uniform inflammable mixture of fire-damp and air ...
occurs throughout any considerable area of a coal mine, but ...
is an instance when a disused heading (or cul-de-sac), in wh...
air was practically stagnant, was slowly fed with fire-damp ...
from the neighbouring strata until, when the fact was dis...
the whole heading had become uniformly filled with a m...
containing 6 per cent. of methane. It has sometimes ha...
also, that the slow ventilating current travelling through a ...
leading from a goaf (or worked-out place) has been found to...
inflammable mixture, uniform in composition through ...
extent. In such cases the dangerous "limit-mixtures" are ...
will allow of self-propagation of flame throughout the ...
mixture, whether ignition occurs at the roof, floor, or centr...
roadway.

The fire-damp of British mines consists of methane ...
varying proportions of nitrogen; also, carbon dioxide, tra...
carbon monoxide and ethylene may be present, and, occas...
traces of ethane have been detected.

This paper records the results of determinations of the ...
and lower-limits of inflammability of mixtures of pure me...
with air, and shows how the compositions of the limit m...

Fig. 2.
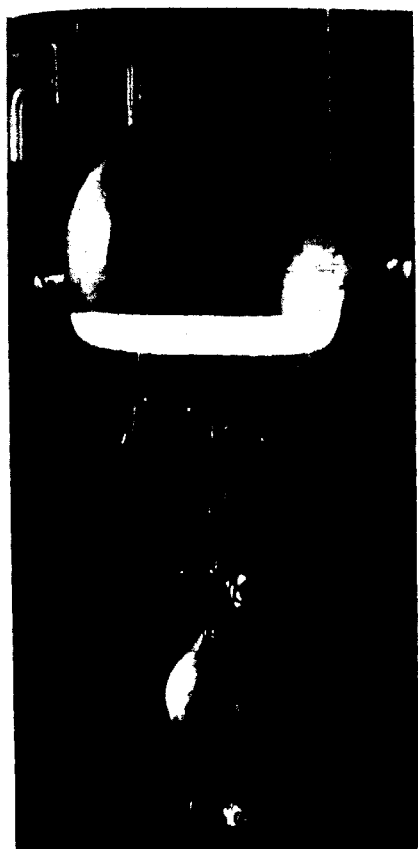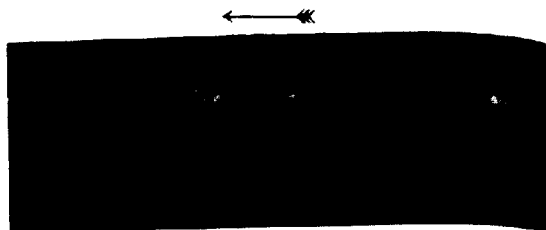
... dependent on the manner in which ignition is effected.[*]
These results are as follows:

	Methane, per cent.	
	Lower limit.	Higher limit.
Vertical ignition in large globe.........	5·6	14·8
Vertical tube, closed at both ends :		
Ignition at bottom [*]	Not less than 5·40	Not more than 14·8
Ignition at top [†]	6·0	13·4
Horizontal tube, closed at both ends :		
Ignited at one end	5·4 (flame travels only along top of tube) 5·6 (methane all burnt)	14·3

[*] ... and Brinsley obtained what appeared to be a self-propagating flame in gas mixture containing, according to analysis, 5·3 per cent. of methane. They were able to repeat the experiment.

[†] The determinations made by Hauser (loc. cit.), using the Le Chatelier burette (upward propagation of flame), were: lower limit 6·05 per cent., higher limit ... per cent. methane. Hauser obtained pure methane from aluminium carbide.

The manner in which the flame travels in the different mixtures is by no means the same, and an attempt has been made to indicate the more striking differences by diagrams. Fig. 1 represents the flame travelling upwards in a closed tube (6 cm. in diameter) containing a 5·4 per cent. methane-air mixture, and Fig. 2 the flame travelling horizontally in a like mixture. Figs. 3 and 4 illustrate the stages in the progress of the flame downwards in a closed tube through a mixture containing 6·0 per cent. of methane.

When an electric spark is passed at the bottom of a closed vessel containing methane-air mixtures with 5·0, 5·1, 5·2, etc., per cent. methane, flares of flame are produced which travel distances increasing with the percentage of methane, until with 5·4 per cent. methane present the distance of travel reaches 2 metres in a tube 2 metres long. It is possible that the flame in a 5·4 per cent. mixture might travel upwards more than 2 metres; it might travel indefinitely, and, on the other hand, it might die out after a distance of 3 metres or less. Since it is obviously impossible to make a crucial experiment to test this point, it must suffice to say that the lower-limit mixture for upward propagation of flame contains not less than 5·4 per cent. of methane. The flame in mixtures containing 5·35 per cent. of methane, contained in a wet glass tube 6 cm. in diameter, never exceeded a distance of about 50 cm.; in 5·3 per cent. and 5·25 per cent. mixtures the flame travelled 40 cm. and 30 cm. respectively.

It will be seen in Fig. 2 that the flame travelling horizontally in

[*] The influence of added nitrogen on the limits, as determined by central ignition in a large globe, is described in a subsequent paper.

a 5·4 per cent. mixture occupies only the upper quarter ... ...
of the containing vessel, and analysis of the mixture left ... ...
6 cm. in diameter after the flame had travelled along it sh...
to contain 3·25 per cent. of methane.   When a tube b... ...
diameter was used, 3·9 per cent. of methane remained ... ...
products of combustion.   Presumably, if a large room ... ...
with such a mixture and a light applied at some point ... ...
floor, a column of flame would travel upwards from the ... ...
ignition to the roof and spread along the upper portion ...
the room.

It may not be generally known that when a slow current ...
containing between 4 and 5 per cent. of methane passes over a s...
flame, such as that of an oil lamp, the cap or aureole that ...
arily forms round the lamp-flame may become detached ...
along with the current.   Similarly, if a slow current of air ...
ing 3 or 4 per cent. of coal gas is allowed to ascend a vert... ...
and a succession of electric sparks passed at the bottom, s... ...
of flame can be caused to pass from end to end of the t... ...
a fraction of the mixture being burnt.

Of a like nature are such mixtures of hydrogen and air as ...
"balls" of flame to travel (perhaps indefinitely) upwards ... ...
them with the convection-currents in the manner dest... ...
Coward and Brinsley.

From the practical point of view such mixtures are not in th...
selves dangerous, but they are potentially dangerous in that ...
could convey flame to richer mixtures.

From the scientific point of view it is of interest to kn...
such curious flames can be produced, but the doubt must ...
remain whether actually "indefinite" propagation of fla...
take place in the mixtures that exhibit them; and the fact ...
chemical reaction proceeds in but a small portion of the ...
mixture, renders it difficult to employ for comparative meas...
ments the "criterion" of inflammability adopted by Coward
Brinsley.[*]

* It should be noted that, making use of their criterion, Coward ...
decided upon 4·1 per cent. as the lower-limit percentage of hy... ...
(3·8 per cent. of hydrogen remaining in the mixture after the flame ha... ...
Dixon and Crofts (this vol., p. 2047) have obtained the following ... ...
ignition temperatures of various mixtures of hydrogen and oxygen :

$2H_2 + O_2$	....	526°
$2H_2 + 2O_2$	....	511
$2H_2 + 8O_2$	....	478
$2H_2 + 16O_2$	....	472
$2H_2 + 32O_2$	....	—

The last mixture, which contained 5·88 per cent. of hydrogen, co... ...
ignited, although five experiments were made in which the temperatures ...

It may be remarked that if the object of their criterion of inflammability is to specify the least quantity of inflammable gas that is capable of propagating flame, that object is not gained. For when a mixture of methane and air containing 5 per cent. of methane, enclosed in a 4 litre globe, is strongly agitated by revolving a small fan therein, and an electric spark passed at the centre of the globe, flame travels rapidly throughout the mixture, all the methane being burnt. The lower limit of inflammability of "agitated" mixtures of methane and air could therefore be stated to be 5·0 per cent., or possibly less with more gently agitated mixtures.

The flame travelling downwards in a 6·0 per cent. mixture, figured in Figs. 3 and 4, and the flame started centrally in a 6 per cent. mixture contained in a large globe, both burn the methane completely. In both cases the line of demarcation between a mixture that will propagate flame and one that will not is sharply marked.[*]

For the latter reason, as well as for their convenience, the criterion of inflammability for downward propagation, used by M. Châtelier and universally applied by French mining engineers in the measurement of fire-damp; and for propagation throughout the mixture, adopted by several investigators, would seem to commend themselves for such comparative measurements as a study of the propagation of flame in gaseous mixtures may demand.

EXPERIMENTAL.

The methane used was prepared from aluminium carbide, and separated from traces of acetylene by passing through ammoniacal cuprous chloride, and from hydrogen by passing slowly over a heated palladium precipitate heated at 90°. It contained 94 per cent. of methane.

The explosion-vessels were glass cylinders, sealed at each end,

<hr/>

[sub-note] ...600°, 700°, 1000°, and 1700° respectively. Dixon and Crofts considered that the limit of inflammability had been passed in the last mixture, but they noted that combustion occurred of part of the mixture.

[*] The following determinations of the lower-limits, downward propagation, were made by Mr. A. Whitaker. With mixtures containing, according to analysis, 6·04 and 6·01 per cent. of methane, flame was propagated throughout the length of a closed tube 7 cm. in diameter and 160 cm. long. With 5·99, 5·98 and 5·95 per cent. of methane the flame travelled 12 or 15 cm. only.

[†] One of mixture sufficient for two experiments was made containing 6·00 per cent. of methane. After one experiment, in which propagation of flame was complete, sufficient air was added to the remainder of the mixture to reduce the percentage of methane to 5·99; flame travelled downwards only 15 cm. in this mixture.

6 cm. in diameter and 2 metres long. They were ...., ..
platinum firing points at one end and at the other w... a ...
way tap, through which the mixtures to be experim..... ...
were introduced after the cylinders had been exhausted ... ..
mixtures were made over glycerol and water in grad..... ...
gas-holders, and were all analysed before use.

EskMeals,
Cumberland.

CCXLII. The Propagation of Flame in ...Li...Mixtures of Methane, Oxygen and Nitrogen.

By Maurice John Burgess and Richard Vernon Wheeler.

In a previous communication (T., 1911, **99**, 2013) we argued ...
"lower limit " mixture (and, similarly, a "higher-limit " ....
is "one such that a given volume must, under the cond...... ...
combustion, evolve just sufficient heat to raise an equa.. . ...
its ignition-temperature."

According to this view, during the propagation of flame ...
"limit " mixture a balance is struck between heat generate..
combustion and heat employed in starting combustion ... ...
with heat "lost " by conduction and radiation.

Theoretically, provided that the amount of energy imparted
the system by the initial source of ignition—an electric spark
example—is small, so that no appreciable impetus to the prop
tion of flame occurs near the source of ignition, flame should tra
throughout a true limit mixture at a uniform speed. Experi...
to be described at a later date, establish the correctness .. .
supposition.

Further, it seems probable that the speed of travel of flame
be the same in all limit mixtures that comprise the same .. ...
ent gases. Experiments show this to be the case so far as flame
propagation in mixtures of methane, oxygen, and nitrogen
concerned.

Limit mixtures thus offer several advantages for the study .. ..
manner of propagation of flame in gaseous mixtures.

This paper contains the results of a series of determinations .. ..
the amounts of methane required to form higher- and low.. ..
mixtures with various "atmospheres ' ranging between air ..
per cent. of oxygen) and a mixture of air and nitrogen contain
13·45 per cent. of oxygen.*

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* The results of preliminary experiments, obtained during the early ... ...
1913, were communicated to the institution of Mining Engineers (T. **44**

The lower-limit mixtures contained a minimum of 5·6 per cent. of methane (when air was used) and a maximum of 6·45 per cent. (when the 13·45 per cent. oxygen "atmosphere" was employed). The minimum value for the higher-limit mixtures was 6·7 per cent. of methane (with the 13·45 per cent. of oxygen "atmosphere") and the maximum value 14·8 per cent. (with air).

The compositions were thus determined of a number of limit mixtures containing widely different proportions of the same three gases methane, oxygen, and nitrogen from which calculations of the heat balances could be made with a reasonable expectation

Fig. 1.

Oxygen in limit mixtures—per cent.

(Y-axis: *Methane in limit mixtures—per cent.*)
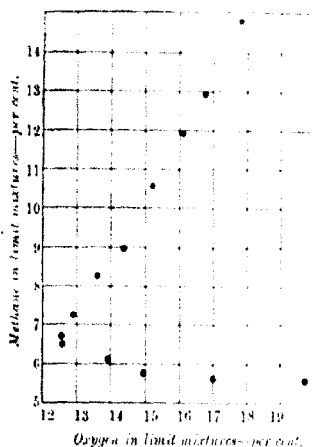
that although errors in calculating the specific heats of the gases and the ignition-temperatures of the mixtures might render the results not strictly accurate, the relative values would be correct.

The results obtained showing the percentages of methane that the limit mixtures with the different "atmospheres" can contain can be given in the form of a diagram (Fig. 1).

In this diagram percentages of methane are plotted against

percentages of oxygen in the limit mixtures. The different atmospheres," with the percentages of methane required in each case to form higher- and lower-limit mixtures, are as follows:

Atmosphere.		Methane, per cent.	
Oxygen.	Nitrogen.	Lower-limit.	Higher-limit.
20·90	79·10 (air)	5·60	14·8?
19·22	80·78	—	12·8?
18·30	81·70	—	11·8?
17·00	83·00	5·80	10·5?
15·82	84·18	5·83	9·9?
14·86	85·14	6·15	8·3?
13·90	86·10	6·35	7·2?
13·45	86·55	6·50	6·7?
13·25	86·75	No mixture capable of propagating flame	

It will be seen that as the oxygen-content of the atmosphere is reduced the higher- and lower-limits come closer together, until with 13·45 per cent. of oxygen only mixtures containing between 6·50 and 6·70 per cent. of methane are capable of propagating flame. A mixture of methane with an atmosphere containing 13·25 per cent. of oxygen is incapable of propagating flame.

Presumably the true "extinctive" atmosphere for methane, the atmosphere in which a jet of methane, however perfectly aerated, would be just unable to burn—contains between 13·45 and 13·25 per cent. of oxygen.[*]

It may be noted that Haldane and Atkinson, who were the first to work on this subject (*Trans. Inst. Min. Eng.*, 1895, 8, 49), found that natural fire-damp could form an inflammable mixture with oxygen and nitrogen when the oxygen present had been reduced to between 12 and 13 per cent. The higher- and lower-limit mixtures of pure methane with the 13·45 per cent. oxygen atmosphere, according to our experiments, contain 12·55 and 12·55 per cent. of oxygen respectively.

The general equation representing the heat balance during the spread of flame in a limit mixture is as follows:

$$(c'M + c''P)(T - t) + q = xQ \quad . \quad . \quad . \quad .$$

where c', c'' represent the specific heats of the mixture (M) and the products of combustion (P) respectively, each at the greatest temperature (T), t being the initial temperature of the mixture, q represents heat dissipated (by conduction and radiation), xQ heat evolved by the combustion of x parts of the combustible gas.

When methane is the combustible gas the calculations are complicated by the fact that combustion is incomplete. Applying

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[*] The extinctive atmosphere for methane is usually regarded as containing 17 per cent. of oxygen; and the "residual" atmosphere—that in which a flame has burnt to extinction—as containing about 15 per cent. of oxygen.

quantities of carbon monoxide occur in the products of combustion of the lower-limit mixtures, whilst with some of the higher-limit mixtures combustion is mainly to carbon monoxide, hydrogen, and steam, and the "water gas reaction" proceeds as the products

Consequently, in order to calculate the heat balance it is necessary to analyse samples of the products of combustion as soon they are formed—before secondary reactions, which can play part in the propulsion of flame through the mixture, have taken

This was done so far as practicable by withdrawing and cooling only small samples of the "flame gases" whilst the flames were rising through the mixtures (which were contained in large globes), in the manner described in the experimental part of paper.

The analyses of these gases show a regular relationship between ratios O_2 : CH_4 in the original mixtures and the proportions of methane that burn completely to form carbon dioxide and steam. In the higher-limit mixtures the ratio O_2 : CH_4 varied from a minimum of 1.20 (in the mixture with air) to a maximum of 1.87 in the mixture with the 13.45 per cent. oxygen ("atmosphere"). The proportion of the methane burned in the former mixture to carbon dioxide and steam was 32.2 per cent.; in the latter mixture was 83.0 per cent. The results have been summarised as follows:

oxygen-content of atmosphere.	Ratio O_2:CH_4 in higher-limit mixture.	Proportions of methane burned to carbon dioxide and steam.
20.90 (air)	1.20	32.2
19.22	1.29	37.8
18.30	1.35	42.6
17.00	1.44	49.0
15.82	1.60	59.0
14.86	1.62	64.5
13.90	1.77	77.4
13.45	1.87	83.0

As the proportion of oxygen to methane is increased, more and more of the latter is completely burned. With a ratio O_2:CH_4 = 1.50 the methane burns to carbon dioxide and half to carbon oxide, whilst when the oxygen present is less than one and a half times the methane present the main reaction is represented the equation:

$$CH_4 + O_2 = CO + H_2 + H_2O.$$
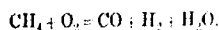
In comparison with these results those obtained by Bone and others with mixtures of methane and oxygen in equal proportions may be quoted (T., 1906, **89**, 676). The percentage composition of the gaseous products of combustion (no carbon was

deposited) averaged: CO_2, 6·3; CO, 41·9; H_2, 50·8, CH...
Commenting on these results, Bone and Drugman say been shown that, below the ignition-point, methane burns at an early stage steam and formaldehyde. The process probably be best expressed as follows:

$$CH_4 \rightarrow CH_3 \cdot OH \rightarrow CH_2(OH)_2 \rightarrow CH_2O + H_2O, \text{ etc.}$$
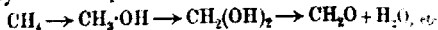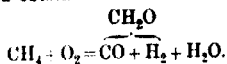
" At high temperatures the formaldehyde would certainly decompose into carbonic oxide and hydrogen, so that in complete combustion we should obtain:

$$CH_2O$$
$$CH_4 + O_2 = \overbrace{CO + H_2} + H_2O.$$

"The 6 per cent. of carbon dioxide formed in our experiment would obviously arise by the secondary interaction of steam and carbonic oxide in the flame."

As a general conclusion from our results, we hold the view that the essential reaction in the propagation of flame in our limit mixtures is that responsible for the formation of carbon monoxide, hydrogen, and steam in equal volumes.

The heat evolved by this reaction is probably almost equally divided between the products of combustion of one "layer" of mixture and the adjoining unburnt "layer"; it is, however, sufficient to raise the unburnt layer to its ignition-temperature. Following rapidly upon this reaction, some of the carbon monoxide and hydrogen is burned, the proportion depending upon the original concentration. The additional heat added to the system in the latter manner enables the nearest unburnt layer to attain its ignition-temperature.

Finally, as the burnt gases cool, the water-gas reaction comes into play, as is shown by comparison of the analyses of the "flame gases" and "final gases" for the same mixture (compare also "The Water-Gas Equilibrium in Hydrocarbon Flames, by G. I. Andrew, this vol., p. 444).

Assuming this to be the correct interpretation of the sequence of events, calculation of the heat balance of each mixture was made, using the data supplied by the analyses of the flame gases.

Calculation having been made of the percentages by weight of the constituent gases of the mixture composed of equal volumes of burnt and unburnt gases, equation (1) can be put in the form

$$(c_{O_2}A + c_{CH_4}B + c_{N_2}C + c_{CO_2}D + c_{CO}E + c_{H_2}F + c_{H_2O}G)(T - t) = xQ + x'Q'_1$$

c_{O_2}, c_{CH_4}, etc., being the specific heats of the respective gases at the temperature $T - t$, and A, B, etc., the percentages by weight of those gases. Of the methane burned, x grams form carbon and

of steam, the heat evolved by the reaction being Q calories per gram; and r' grams form carbon monoxide, hydrogen, and steam, the heat evolved by the reaction being Q' calories per gram.*

Some doubt attaches to the value which should be assigned in each case to T, the ignition temperature of the mixture. Tables of the "ignition-temperatures" of various gases do not, in the majority of cases, afford information as to the percentage composition of the mixture formed by the combustible gas with air (or oxygen) when ignition occurs. Thus, the experiments of Dixon and Coward (T., 1909, **95**, 514), in which a heated jet of the combustible gas was allowed to flow into a heated atmosphere of air or oxygen, only determined for each gas the ignition temperature of a mixture having (presumably) the lowest ignition temperature, without showing the composition of that mixture.

In a recent paper by Dixon and Crofts (this vol., p. 2036) the ture ignition-temperatures of different mixtures of hydrogen and oxygen, determined by the method of adiabatic compression suggested by Nernst, are given, and it appears that increased oxygen concentration is accompanied by decreased temperature of ignition. A similar conclusion for methane-air mixtures may be drawn from the experiments of Taffanel and Le Floch (*Compt. rend.*, 1913, **157**, 469); so long as the ratio O_2/CH_4 was greater than, or not much less than 2.0, the ignition-temperatures of the mixtures were the same; a continued increase in the methane-concentration, however, was accompanied by a regular increase in the ignition-temperatures of the mixtures.

Using this relationship between oxygen-concentration and ignition-temperature, established by Taffanel and Le Floch, we have calculated the ignition-temperatures of our mixtures, taking Dixon and Coward's lowest figure as being probably most nearly correct for mixtures having ratios O_2/CH_4 2.0 or more.† The temperature range between $650°$ for such mixtures and $715°$ for the

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* The values employed in our calculations are: for the reaction $CH_4 + 2O_2$, $23,800$, Q $11,910$ calories per gram; for the reaction

$$CH_4 + O_2 = CO + H_2 + H_2O,$$
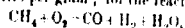
Q' calories per gram. For the specific heats (at constant volume) we have the following determinations:

Oxygen	0.1548	0.000023t
Methane	0.4501	0.000016t
Nitrogen	0.1677	0.000016t
Carbon dioxide	0.1531	0.000059t
Carbon monoxide	0.1730	0.000016t
Hydrogen	2.4020	0.000016t
Steam	0.3300	0.000120t

† Taffanel and Le Floch, in their determinations, did not adequately allow, as did Coward, for the influence of heated surfaces.

mixture having a ratio $O_2/CH_4 = 1\cdot20$ (the higher-limit mixture with air).

The results of the calculations are shown in Fig. 2, where q, the heat evolved, is plotted for each limit mixture against q, the heat unaccounted for or "lost." It will be seen that the two are practically proportional, the heat unaccounted for averaging for each mixture 35 per cent. of the total evolved.

This heat-loss, the magnitude of which is no doubt due to the fact that the accumulation of sufficient energy for the propagation of flame is a prolonged process—the combustion of methane takes place "by stages," * is necessarily made up of loss by (1) conduction and convection, and (2) radiation.

The number of calories transmitted by the flame to any given distant layer of unburnt gas by conduction and convection may be

Fig. 2.

$Q = $ Large calories.
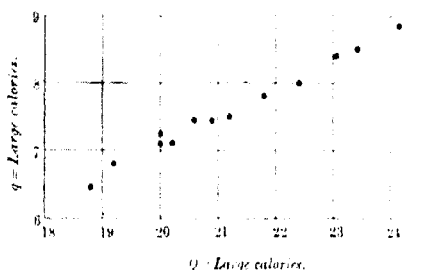
regarded as approximately proportional to the difference in temperature between the two, and a curve representing the transmission of heat by flames of different temperatures would be, as nearly as possible, a straight line.

As regards heat transmitted by flames as radiant energy—it will be it noted, has been found in the case of non-luminous coal-gas flames, 30 mm. in diameter, may amount to as much as 20 per cent. of the whole heat of combustion †—the effect of temperature is more difficult to estimate. Callendar suggests that Planck's equation for a single wave-length may be assumed, and for a Bunsen flame of mean wave-length $3\cdot5\,\mu$, gives the following table of approximate values for the variation in intensity of

* The well-known "lag" in the ignition of methane is also explicable on this cause (compare T., 1911, **99**, 2020).

† Third Report, Gaseous Explosions Committee, British Association, 1914.

temperature, for comparison with the fourth power law of Stefan for the radiation of a black body:

Absolute temperature ...	$1000°$	1500	$2000°$	$2500°$	$3000°$
Radiation, Planck.	0·016	0·059	0·142	0·233	0·331
Radiation, Stefan.	0·009	0·045	0·142	0·347	0·721

Commenting on this table, Callendar says: "The rate of variation, according to Planck's formula for a single wave length, is much slower than the fourth-power law, and tends in the limit to be directly proportional to the absolute temperature at high temperatures. The actual rate of variation should be between these limits, but nearer to Planck, *unless carbon begins to separate in such mixtures at high temperatures*." [*]

As already noted, q, the "loss" of heat from our mixtures (in none of which did carbon separate), is practically directly proportional to Q, the total heat evolved.

EXPERIMENTAL.

The different mixtures of oxygen and nitrogen were made in large glass gas-holders holding sufficient for a dozen or more experiments, and the limit mixtures with methane prepared from them in smaller gas-holders over glycerol and water.

The method of determining the limits, and the apparatus employed, were similar to those described in our previous paper (*loc. cit.*, pp. 2020—2024). The methane used was prepared from aluminium carbide, and was purified from traces of acetylene by passing through ammoniacal cuprous chloride, and from hydrogen by passing slowly over "oxidised" palladium precipitate heated to 13°. It contained 99·7 per cent. of methane.

Each mixture was analysed, the methane being determined by explosion (with electrolytic gas or excess of air and oxygen added as the case might require), and the oxygen by absorption by strongly alkaline pyrogallol.

A large number of experiments with each atmosphere were made where the limits were fixed as closely as was desired. Corresponding mixtures were then carefully prepared and inflamed in a special form of explosion-vessel designed for securing a sample of the "flame gases" whilst the flame was travelling (Fig. 3, p. 2592).

This explosion-vessel was a 2½-litre globe, with glass-covered electrodes reaching to the centre. Through the side of this globe are fused, in the positions shown in the photograph, two fine capillary tubes, either of which could make connexion, through a three-way tap, with a small bulb filled with mercury to within 3 c.c. of its capacity. The space above the mercury in this small

[*] Third Report, Gaseous Explosions Committee, British Association, Appendix A.

Per cent. by volume.

Oxygen-content of atmosphere	Description of limit mixture	Analyses of limit mixture.			Analysis of flame gases.						Analysis of final gases.						Calories.	
		O_2	CH_4	N_2	CO_2	O_2	CO	H_2	CH_4	N_2	CO_2	O_2	CO	H_2	CH_4	N_2	Q	q
20·90 (air)	Higher	17·80	14·82	67·38	4·80	nil	10·10	10·50	0·85	73·75	4·99	nil	8·71	10·74	2·05	73·52	24,150	8850
19·22	"	16·74	12·93	70·33	5·00	nil	8·19	8·19	0·72	77·91	5·32	nil	7·69	7·87	1·59	77·52	23,400	8500
18·30	"	16·12	11·91	71·97	5·37	nil	7·23	7·26	0·82	79·32	5·55	nil	5·95	6·25	1·70	80·55	23,050	8400
17·00	"	15·22	10·55	74·23	5·55	nil	5·78	5·75	0·38	82·54	5·68	nil	5·68	5·20	0·56	82·82	22,400	8000
15·82	"	14·40	8·96	76·64	6·03	nil	4·19	2·93	0·25	86·62	6·43	nil	3·18	2·81	0·59	86·96	21,800	7800
14·86	"	13·59	8·36	78·05	6·27	nil	3·46	2·66	0·34	87·38	6·39	nil	2·96	2·53	0·26	87·86	21,200	7500
13·90	"	12·88	7·26	79·86	6·41	nil	1·87	1·20	0·37	90·15	6·52	nil	2·34	0·98	0·35	89·82	20,900	7450
13·45	"	12·55	6·70	80·75	6·62	nil	1·36	nil	0·55	91·32	6·92	nil	0·83	nil	0·06	91·28	20,200	7100
13·45	Lower	12·57	6·50	80·93	6·82	nil	1·31	0·35	0·35	91·17	6·03	nil	0·47	nil	0·29	92·31	20,000	7100
13·90	"	13·00	6·35	80·65	6·57	0·56	0·00	0·45	nil	91·82	7·27	0·34	nil	nil	nil	92·39	20,600	7450
14·86	"	13·95	6·15	79·90	6·46	1·54	0·48	0·18	nd	91·34	7·00	1·90	nil	nil	nil	91·10	20,000	7250
15·82	"	14·89	5·83	79·28	6·23	3·43	0·32	0·10	nil	89·92	6·60	3·65	nil	nil	nil	89·75	19,200	6800
20·90 (air)	"	19·73	5·60	74·67	6·25	9·65	0·07	nil	nil	84·03	6·30	9·58	0·05	nil	nil	84·07	18,800	6450

vessel was thoroughly exhausted of air, and served, when the three-way tap was rapidly opened, to capture a sample of the gases at either of the two points where the capillary tubes ended within the explosion-vessel. When the whole apparatus was inverted this sample could be withdrawn, by means of a mercury pump, through the tap shown at the bottom of the photograph.

In all the limit mixtures the manner in which the flame travelled was the same. So soon as the igniting spark had been passed a tongue shot up to the top of the vessel, bent over, and, after thus filling the whole of the top quarter of the globe, travelled downwards to the bottom as a uniform layer of light blue colour.* This layer had an apparent thickness of between 1½ and 2 inches, and travelled sufficiently slowly to enable the tap leading to the sampling vessel to be manipulated at the right moment.

The moment chosen for all the samples of which analyses are given in this paper was when the layer of flame had passed half way past the end of the upper capillary tube, as indicated in fig. 3 by the shading added to the photograph, which gives a very fair idea of the appearance of the flame when observed through the side of the globe at the moment of sampling.

The gases were driven into the sampling-vessel under pressure of between 2 and 3 atmospheres, so that, although the space in that vessel unoccupied by mercury was under 5 c.c., between 10 and 15 c.c. of gases were obtained for analysis.

Samples of the products of combustion remaining in the explosion vessel were withdrawn for analysis after sufficient time had been allowed for complete mixture.

Results of Experiments.—The compositions of the limit mixtures, and the analyses of the "flame gases" and "final gases" are given on p. 2604.

A correction has been introduced in the analyses of flame gases for the unburned mixture contained in the capillary tube leading to the sampling-vessel.

The last two columns in the table record the calculated values of l and q plotted in Fig. 2.

These results have already been discussed in the theoretical section of this paper. An additional point that should be noted is the preferential burning of hydrogen over carbon monoxide in all the mixtures that contain a ratio O_2/CH_4 greater than 1·5.

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† In some of the higher-limit mixtures the flame had a slightly reddish tinge.

CCXLIII.—*The Propagation of Flame in Mixtures of Methane and Air. The "Uniform Movement"*

By RICHARD VERNON WHEELER.

IN the course of their well-known researches on the combustion of explosive gaseous mixtures, Mallard and Le Chatelier (*Ann. des Mines*, 1883, [viii], **4**, 274) studied the propagation of flame in mixtures of methane and air contained in horizontal tubes. So far as such mixtures are concerned, the general conclusions drawn by them regarding the manner in which flame is propagated were as follows.

When the mixture contained in a horizontal tube closed at one end and open at the other is ignited at the open end, the flame travels for a short distance at a uniform speed. This "uniform movement" is followed by a "vibratory movement," in the course of which the flame travels backwards and forwards in an irregular manner, the mean speed from point to point along the tube being usually greater than that of the "uniform movement." These vibrations usually continue to the end of the tube, but sometimes during a particularly violent vibration the flame may be extinguished, owing to the mixing of burnt gases with the unburnt mixture.

When the mixture is ignited at the closed end of the tube the flame travels, in short tubes at all events, with increasing speed towards the open end.

In the course of investigations on mine explosions, carried out in the first instance, for the Mining Association of Great Britain, and, latterly, at the Home Office Experimental Station, the necessity arose for repeating Mallard and Le Chatelier's experiments regarding mixtures of methane and air.

The present paper deals with the "uniform movement," the speed of which is the normal speed of propagation of flame by conduction of heat from layer to layer of the mixture, and is constant for a given mixture at a given temperature and pressure.

Mallard and Le Chatelier made a complete study of how far the diameter, length, and material of the tubes influenced the speed and duration of the uniform movement in many gaseous mixtures with the object of determining the limiting dimensions required to ensure that the true speed—the speed that would be obtained in a mixture of indefinite extent—should be determined. Given the right dimensions of tubes, the material of which they were made did not appreciably affect the speeds. Repetition of Mallard

and Le Chatelier's experiments regarding these experimental condi-
tions has confirmed their results.

The diameter of tube necessary to avoid cooling by the walls,
and consequent retardation of the flame, was found to be greater
the slower the speed of the flame. For the most slowly moving
flames in mixtures of methane and air a tube of at least 5 cm.
diameter is necessary. The speed of travel of flame in a tube 9 cm.
in diameter is slightly greater than in a tube 5 cm. in diameter.

The duration of the uniform movement, which varies with each
mixture, increases with the diameter and length of the tube up to
a certain maximum, after which increase in length makes no appre-
ciable difference. In a tube 5 cm. in diameter and 6 metres long
the uniform movement in all mixtures of methane and air extends
over a distance of about 150 cm., whereas in a tube of the same
diameter and 2 metres long the distance travelled by the flame at
a uniform speed may be less than 50 cm.

For their experiments Mallard and Le Chatelier used tubes
5 cm. in diameter and 1 metre long, and measured the speed of
travel of flame over the first 50 cm. The length of the tube was
insufficient to ensure that the measurements of the speed of the
flame would not include part of the "vibratory movement," a fact
which they themselves realised (*loc. cit.*, p. 317). Their measure-
ments for the same mixture show, in consequence, rather wide
variations. Their experiments were further vitiated by the fact
that the methane used was prepared from sodium acetate ("il
exhalait une forte odeur d'acetone "). Such methane may
contain as much as 10 per cent. of nitrogen, 10 per cent. of
unsaturated hydrocarbons, and 2 or 3 per cent. of hydrogen.[*]

The conclusions drawn by Mallard and Le Chatelier were :

(1) The speed of the uniform movement increases regularly with
the percentage of methane up to a certain maximum, after which
it decreases regularly. The curve obtained on plotting speeds as
ordinates and percentages of methane as abscisse is thus repre-
sented by two straight lines meeting at a point. Their curve
(from Plate VIII of their paper) is reproduced in Fig. 1.

(2) The maximum speed is obtained, not with that mixture
containing the quantity of methane required for complete com-
bustion, namely, 9·4 per cent., but with a mixture containing
about 12 per cent. of methane. Le Chatelier ("Leçons sur le
carbone," Paris, 1908) explains this result by assuming that the
speed of propagation of flame during the uniform movement
depends, not only on the temperature of combustion of the mixture,
but on its thermal conductivity, which is greater the greater the

* Compare Hauser, " Leçons sur le grisou." Madrid, 1908.

proportion of methane present. The thermal conductivit$_{\text{ies of air}}$
and of methane are $5\cdot22 \times 10^{-5}$ and $6\cdot47 \times 10^{-5}$ respectively.

Fresh determinations, made in the manner described in the
experimental portion of this paper, do not bear out Mallard and
Le Chatelier's results. The form of curve obtained on plotting
speeds as ordinates and percentages of methane as abscissæ is
shown in Fig. 1.

It will be seen that there is practically no difference between the
speeds attained in mixtures containing from 9·45 to 10·55 per
cent. of methane,* such differences as there are being probably
within the limits of experimental error.

Near the lower- and higher-limits of inflammability, which for
horizontal propagation, are 5·4 and 14·3 per cent. respectively, the

Fig. 1.

Methane in firedamp-air mixture, per cent.
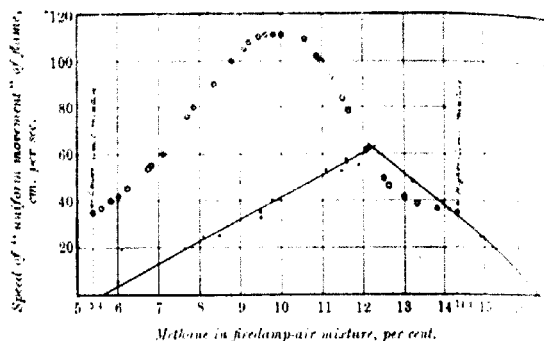
curve flattens, more noticeably towards the higher limit, and
becomes, ultimately, nearly horizontal. It will be understood,
therefore, that a prolongation of either "limb" of the curve, so
as to cut the zero velocity ordinate, as done by Mallard and
Le Chatelier to determine the theoretical limits of inflammability,
is not justifiable.

Vibrations were not developed by the flames in all the mixtures.
In those containing more than 12·5 or less than 5·8 per cent. of
methane the flame usually travelled at a uniform or slightly decreas-

* This conclusion is confirmed by another series of experiments in which
different mixtures of methane and air were ignited at the centre of a large spherical
explosion vessel. The time that elapsed between the moment of ignition and the
first indication of pressure on the sides of the vessel was less the higher the per-
centage of methane in the mixture up to 9·5 per cent. methane, after which it
remained practically constant up to 11 per cent.

the speed throughout the length of the tube, although sometimes slight vibrations were noticeable in all but the "limit-mixtures." In these latter the speed of travel of flame was quite uniform throughout, and was the same for both the higher- and lower-limit mixtures.

As noted in a previous paper (this vol., p. 2593), the flame

Fig. 2.
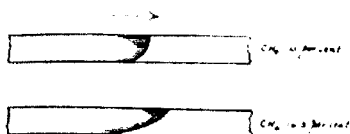
travelling horizontally in a 5·4 per cent. methane-air mixture, contained in a tube 5 cm. in diameter, occupies only the upper part of the tube. The flames in the other mixtures of methane and air, including the higher-limit mixture, completely filled the cross section of the tube, the front of the flame (during the uniform

Fig. 3.
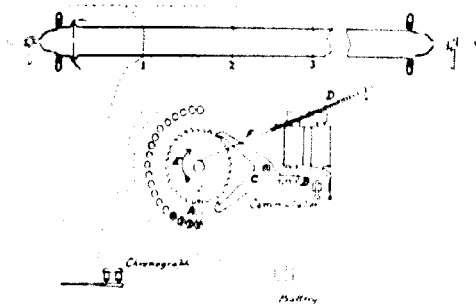
movement) being shaped as shown in Fig. 2. The faster the speed of the flame the blunter was its front.

EXPERIMENTAL.

The arrangement of glass tubes is shown in Fig. 3. Three lengths of tube of 5 cm. internal diameter, each 2 metres long, were joined together by broad pieces of stout rubber tubing, and supported horizontally in a straight line. Each end of the complete length

of 6 metres was flanged and ground to receive flanged end pieces
which were held in position by metal clips. Each end piece was
fitted with a wide-bore three-way tap. Glass-covered platinum elec-
trodes reaching to the centre of the tube, leaving a spark gap of
3 mm., were fused 4 cm. from one end.

Another tube, similarly arranged, but of 9 cm. internal
diameter, was used for a separate series of experiments.

"Screen-wires" of copper 0·025 mm. in diameter were threaded
vertically across the tube through fine holes pierced through the
walls at certain points, the holes being afterwards covered by
adhesive plaster. In order to avoid including in the measurement
of the speed of the flame any impetus that might be given by the
igniting spark, the first screen-wire was fixed 40 cm. from the point
of ignition. Other screen-wires were fixed 50, 100, 200, 300 and
400 cm. respectively from the first.

The method of recording the time of passage of flame along the
tube was electrical. Each screen-wire carried a small electric
current, the interruption of this current when the flame melted
the wires being recorded by the movement of an electro-magnet.

It was important to avoid error due to latency or "time-lag" of
individual electromagnets. An instrument, which can be termed
an automatic commutator, was therefore designed to enable each
successive break in circuit to be recorded by the same electromagnet.
This instrument is operated in the following manner:

One terminal of the battery supplying the electric current is
connected to the brush, A, of the commutator (Fig. 3), and a lead
from the other terminal of the battery conducts the current to the
electromagnet of the chronograph, so that its armature is attracted.
The current then passes by a lead to the electromagnet on the
commutator, and that armature is also attracted; the lead carrying
the current then goes to one terminal of the screen-wires one by
explosion-tube one after the other; the other terminal of each
screen-wire is connected to the corresponding stud on the commu-
tator by separate leads.

Supposing the brush, A, to be resting on No. 1 stud (the position
that it occupies at the beginning of an experiment), the current is
then flowing through the chronograph electromagnet, the commu-
tator electromagnet, and No. 1 screen-wire; then through the
brush, A, back to the battery. Suppose now that the flame passes
along the tube and melts screen-wire No. 1; the chronograph
electromagnet releases its armature, and the pen it carries makes
a mark on the moving surface; at the same time the armature, B,
of the commutator electromagnet is released, and the anchor
escapement, C, attached to the armature, is moved. This allows the

and spring, *D*, to pull the scape-wheel, *E*, round by the cord, *F*, which is wound on a drum attached to the axis of the scape-wheel. brush, *A*, then moves on to stud No. 2, and the current at begins to flow through screen-wire No. 2; the chronograph electromagnet and the commutator electromagnet, and the armature of both these are again attracted; the pen on the chronograph is moved back to its former position, as also are the armature, and the escapement, *C*, whilst the brush, *A*, moves a little further on to stud No. 2. When the flame reaches No. 2 screen the same cycle is repeated and so on for as many screens as be required, all the interruptions of circuit being recorded by one pen on the chronograph.*

The chronograph used was the laboratory chronograph of the Cambridge Scientific Instrument Company, the speed of travel of moving surface (a spool of Morse paper) being recorded by a second contact-clock.

Method of Conducting an Experiment. The mixtures of methane and air were made in a 140-litre gas-holder over water rendered slightly alkaline by potassium hydroxide. A rapid rent of the mixture was passed through the explosion-tube until gases entering and leaving had the same composition, as shown explosion-analyses of samples taken through the three-way taps. volume of mixture equal to about six times the volume of the was found to be ample for sweeping out all the air contained the tube.

All electrical connexions through the screen-wires and chronograph having been established, the left-hand end-piece of the explosion tube was removed (by sliding it downwards) and the mixture ignited at the now open end by passing an induction-coil it.

The methane used was a particularly pure supply of fire-damp from a "blower" at a colliery in South Wales, whence it was and compressed in cylinders. Analysis, after removal of per cent. of carbon dioxide, showed it to contain 97·4 per cent. methane, 2·3 per cent. of nitrogen, and 0·3 per cent. of other unties (carbon monoxide and ethylene). It contained no hydrogen or ethane.

* A somewhat detailed description of this device has been given in the belief that it may prove of value to other workers. The author has found it adequate for timing the speed of the rapidly moving flames of coal-dust explosions and coal-gas and air explosions in large galleries. Its effectiveness depends essentially on rapidity with which the brush of the commutator can be made to move from stud to the next; by suitable proportioning and adjustment of the moving and regulation of the electric current passing through the magnets, the time for the brush to move from stud to stud can be made as little as $\frac{1}{100}$th second.

Results of Experiments.—The results of all the determinations made of the speed of the uniform movement in different mixtures are given in the table that follows. As a general rule, the uniform movement extended for a distance of 150 cm. from the point of ignition, so that from each experiment with a particular mixture two determinations of the speed were obtained (between No. 1 and No. 2, and between No. 2 and No. 3 screen-wire respectively. Some of the more rapidly-moving flames, in mixtures containing between 9·5 and 11·0 per cent. of methane, began to vibrate just before reaching the third screen-wire; in such cases only the speed between screen-wires Nos. 1 and 2 was taken as being that of the uniform movement.

Methane in fire-damp air mixture, per cent.	Speed of " uniform movement " of flame, cm. per second.
5·40	36·5, 36·0, 35·5, 35·5, 35·5, 35·5, 36·0, 35·5.
5·60	37·0, 37·0.
5·85	40, 40·5, 40·5, 40·5.
6·25	46, 46, 45·5, 45, 45·5, 45, 45·5
6·75	54, 54.
6·80	56, 55, 55, 55.
7·10	61, 59, 61, 59.
7·70	77, 77, 75, 75.
8·35	91, 90.
8·80	100, 100, 99, 100.
9·10	105, 104, 106, 104.
9·20	108, 109.
9·45	110, 110, 110, 110.
9·60	111, 111.
9·80	111, 112.
10·00	112, 110, 112, 113, 112, 110, 109, 113
10·60	109, 109, 109.
10·90	102, 102, 101.
11·00	100, 98, 99, 99.
11·20	93, 92.
11·50	84, 84, 83, 83, 85, 84.
12·10	62·5, 62.
12·50	50, 50, 49.
12·65	49, 47, 48, 46.
13·00	42·5, 42, 42, 42.
13·05	41, 40·5.
13·30	39, 38, 39, 38, 38, 38, 38.
13·80	37, 36·5.
14·30	36·0, 35·5, 35·5.

For the determinations of the speed of travel of flame in higher-limit mixture pure methane was used, since the 2·3 per cent of nitrogen contained in the fire-damp slightly affected the higher limit, whereas it had no appreciable effect on the speed of travel of flame in the other mixtures (compare this vol., p. 2596).

A similar series of determinations was made, using an explosion tube of 9 cm. internal diameter. The speeds were from 5 to 10 per second greater than those of corresponding mixtures in tube 5 cm. in diameter. The shapes of the curves connecting the

in percentages of methane, and the limits of inflammability, were same in both series of experiments.

The propagation of flame in mixtures of methane and air, and mixtures to which nitrogen has been added, has been further aird. An account of the work will be communicated later to , Society.

Addendum.

Since this paper was prepared an account has appeared of experiments on the same subject by A. Parker and A. V. Rhead (this ... p. 2150). It is surprising to find that these authors are apparently unacquainted with Mallard and Le Chatelier's complete researches dealing with the "uniform" and "vibratory" movements during the propagation of flame in gaseous mixtures contained in glass tubes, as outlined in the present paper. Their results are interesting in that they emphasise the necessity, pointed out by Mallard and Le Chatelier, of employing tubes of ample diameter when conducting experiments of this nature; the tubes used were of too small a diameter to enable them to determine either the true character of the speed-percentage curve or the limits inflammability.

ERNEST S.,
CUMBERLAND.

XLIV.—*Volatile Oil from the Leaves of* Barosma venusta.

By ERNEST GOULDING and OSWALD DIGBY ROBERTS.

THE genus *Barosma*, of which about thirty species exist in South Africa, derives its chief importance from the fact that certain species yield the so-called Buchu leaves, which are employed in medicine as mild disinfectants of the urinary tract. The physiological activity of the leaves is principally due to the volatile oil which they contain. The source of Buchu leaves of the British Pharmacopœia, or "short Buchu," is *Barosma betulina*, Bartl. and Wendl., but the leaves of *B. crenulata*, Hook. and *B. serratifolia*, Willd., are also met with in commerce under the name of "long Buchu."

Another species of Barosma, *B. venusta*, Eckl. and Zeyh., occurs in considerable quantities in the Uitenhage District of the Cape Colony. Information was desired in South Africa as to the possible value of the leaves of this plant in comparison with Buchu

leaves, and an examination of the material was therefore undertaken at the Imperial Institute.

The most characteristic constituent of the oil of *Barosma betulina* is diosphenol, which is present in quantities of 20—30 per cent.; the oils of *B. crenulata* and *B. serratifolia*, however, contain only a very small proportion of this substance. The results of the present investigation show that the oil of *B. venusta* differs very considerably in odour and composition from that of Buchu leaves in that it does not contain any diosphenol.

In 1911 a sample of the leaves of *Barosma venusta* was received at the Imperial Institute from the Cape Province, South Africa. On distillation in a current of steam it yielded 2·7 per cent. of volatile oil, which was of a lemon-yellow colour and pleasant odour, and had D^{15} 0·877 and α_D^{20} 1°4' in a 100-mm. tube.

A larger consignment of the leaves, forwarded in 1912 furnished 2·0 per cent. of volatile oil with the following constants:

D^{15}	0·865
α_D^{20} in 100 mm. tube	+ 0·47
Acid value	5·6
Ester value	6·2

    (Corresponding with 2·2 per cent. of esters, calculated as $C_{10}H_{17}·OAc$.)

Ester value after acetylation 55

    (Corresponding with 15·7 per cent. of total alcohols, or 14·3 per cent. of free alcohols and 2·2 per cent. of esters.)

Fractional Distillation of the Oil.

On distilling the oil under atmospheric pressure the following fractions were obtained, but some decomposition occurred:

Fraction.	Per cent.	Boiling point.	D^{15}.	α_D in 100 mm. tube.
I.	44	163—190°	0·8100	inactive.
II.	17	190—205	0·8932	inactive.
III.	28	205—230	0·9531	+ 0·30'
IV.	9	230—245	0·9610	liquid too dark coloured to admit of this determination.
Residue	2	—	—	

Isolation and Identification of Myrcene.

When a portion of the oil was distilled under 60 mm. pressure about 48 per cent. collected between 83° and 88°. This fraction after being treated repeatedly with sodium and redistilled, had D^{15} 0·8060, and was optically inactive; it distilled at 165° under atmospheric pressure, but suffered partial decomposition

This hydrocarbon exhibited the properties characteristic of myrcene, for which the following constants have been recorded:

Power and Kleber [1]	D^{14} 0·8023	b. p. 167°.
Semmler [2]	—	b. p. 171—172°.
Chapman [3]	D^{15} 0·8046	b. p. 166–168°.
Enklaar [4]	D^{11} 0·8013	b. p. 166—168°.
Semmler and Mayer [2]	D^{30} 0·7937	...

Pharm. Eentralh., 1895, **13**, 61.

[2] *ib.* 1903, **83**, 507.

[3] *Ber.*, 1911, **44**, 2010.

[2] *Ber.*, 1901, **34**, 3216.

[4] *Diss.*, Utrecht, 1905.

The terpene showed a great tendency to resinify, and readily combined with four atoms of bromine. On reduction with sodium and alcohol it was converted into a compound having D^{15} 0·7860, a value which agrees well with those recorded for dihydromyrcene, namely, 0·7802 and 0·7852, by Semmler (*loc. cit.*) and Enklaar (*loc. cit.*) respectively. This reduction product furnished a tetrabromide, melting at 91°, which crystallised from methyl alcohol in long, white needles. The melting point of dihydromyrcene tetrabromide has been given as 87° by Semmler and Mayer (*loc. cit.*) and 88° by Enklaar (*loc. cit.*). By the action of a mixture of glacial acetic acid and sulphuric acid on the original terpene, an acetate was obtained which resembled linalyl acetate in odour, and, on hydrolysis, yielded an alcohol. This alcohol, when oxidised with chromic acid, did not furnish citral, but the odour of the product suggested the presence of some other aldehyde. These observations accord with those of Barbier (*Compt. rend.*, 1901, **132**, 1048) on the oxidation of myrcenol. The existence of myrcene in the oil is therefore established.

Aldehydes : Identification of Anisaldehyde.

A portion of the oil was shaken with solution of sodium hydrogen sulphite. After the aqueous liquid had been separated and washed with ether, it was rendered alkaline by the addition of sodium carbonate, and extracted by repeated agitation with ether. The ethereal solution was dried with anhydrous sodium sulphate, and the ether was removed by distillation The residue, amounting to about 0·5 per cent. of the original oil, appeared from its taste and odour to consist chiefly of anisaldehyde, and, on oxidation with potassium permanganate, was readily converted into anisic acid, which after recrystallisation melted at 183—184° (anisic acid has m. p. 184°).

Alcohols: Indication of the Presence of Linalool.

The fraction boiling at 190—205° under atmospheric pressure consisted largely of alcohols, and had a sweet odour resembling that of linalool; on oxidation it yielded citral, which was characterised by its odour and by the preparation of α-citryl-β-naphtho-cinchoninic acid, melting at 199°. It is therefore probable that the alcohols consist in part of linalool.

Phenols: Absence of Diosphenol.

When the original oil, after being washed successively with sodium carbonate solution and sodium hydrogen sulphite solution to remove acids and aldehydes, was treated with 5 per cent. solution of sodium hydroxide, an absorption amounting to only 0·2 per cent. took place. On acidifying the solution and extracting with ether, a phenolic substance was obtained, but in too small a quantity to admit of investigation; this product did not give any distinctive coloration with ferric chloride. No evidence could be obtained of the presence of diosphenol.

Ethers: Identification of Methylchavicol.

A fraction of the oil, boiling at 213—218°, was found to consist of methylchavicol, which was identified in the following way.

The fraction was heated with 20 per cent. alcoholic potassium hydroxide solution for two days in a sealed tube at 200°. The contents of the tube were diluted with water and extracted with ether. After drying the ethereal solution with anhydrous sodium sulphate, and removing the ether by evaporation, it was found that the oil had been converted almost quantitatively into anethole which boiled at 232—234°, and solidified on cooling to a mass of crystals, melting at 22°. The product possessed the odour and sweet taste characteristic of anethole. Determinations of methoxyl in the original oil gave results indicating the presence of 21·4 per cent. of methyl ethers (calculated as methylchavicol):

0·2770 gave 0·0947 AgI. OMe = 4·51 or $C_9H_9 \cdot OMe = 21·5$ per cent.
0·2895 „ 0·0980 AgI. OMe = 4·46 „ $C_9H_9 \cdot OMe = 21·3$ „

Constituents of High Boiling Point.

The fraction which distilled at 230—245° was brownish-yellow, viscous, and had a somewhat empyreumatic odour; it probably contained sesquiterpenes, together with polymerides and decomposition products of myrcene, due to the high temperature to which it had been heated.

Summary of Results.

The results of this investigation indicate that the volatile oil of *Laurus cinnamon cinnusta* leaves has approximately the following composition:

	Per cent.
Hydrocarbons, chiefly or entirely myrcene	43·0
Aldehydes, „ „ „ anisaldehyde	0·5
Phenols	0·2
Phenol ethers, methylchavicol	21·4
Alcohols, partly linalool (calculated as $C_{10}H_{17}\cdot OH$)	14·3
Esters (calculated as $C_{10}H_{17}\cdot OAc$)	2·2
Sesquiterpenes, loss, etc. (by difference)	18·4

In conclusion, reference may be made to an examination of the oil by Jensen (*Pharm. J.*, 1913, [iv], **36**, 60). Although the leaves from which he distilled the oil were obtained from the same source as those used in the present investigation, the results show certain differences, of which the most remarkable is that he found 5 per cent. of chavicol, whereas the authors have not been able to detect the presence of even a trace of this phenol.

XLV.—Sodium Amalgams: Specific Volumes and Electrical Conductivities.

By ERNEST VANSTONE.

account has already been given of the investigation of the thermal diagram and the determination of the specific volumes of solid and liquid sodium amalgams (*Trans. Faraday Soc.*, 1911, **7**,

t was shown that when specific volume was plotted against concentration of amalgam expressed in atomic percentages, smooth curves were obtained, although the corresponding thermal diagram showed many discontinuities.

Since the publication of the first paper, the specific volumes have been plotted against concentrations expressed in percentages by weight. It was shown by Maey (*Zeitsch. physikal. Chem.*, 1899,

29, 119) that the specific volume of alloys is a linear function of the concentration expressed in percentages by weight, better the new volume-concentration diagram (Fig. 1) consists of a set of straight lines, having nearly the same obliquity, and confirms the existence of inter-metallic compounds shown by the thermal diagram.

The concentrations (in atomic percentages of sodium) where the

Fig. 1.
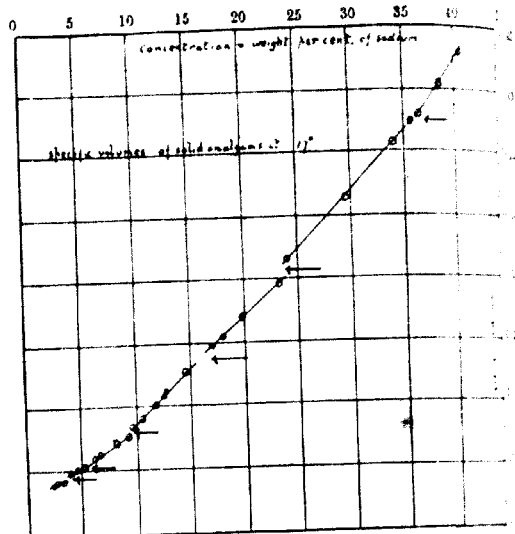
discontinuities occur are given below; those obtained by the thermal method are given for comparison.

Concentrations.

Weight per cent.	Atoms per cent.	Atoms per cent. (thermal)
36·0	83·0	85·2 and 83·4
23·6	73·5	73·5
16·4	63·0	63·3
9·4	47·5	47·5 and 32·5
5·2	32·5	33·3
2·8	20·0	17·9

When the comparative slope of the lines in Fig. 1 is noted and the fact that the concentrations have to be read in the diagram in percentages by weight and then transferred

these percentages, the agreement between columns (2) and (3) in the above table is as satisfactory as can be expected.

The Constitution of Liquid Amalgams.

Many researches have been carried out on liquid amalgams, having for their object the determination of the molecular complexity of metals in amalgams rich in mercury.

Measurements of (1) vapour pressure, (2) E.M.F., and (3) lowering of freezing point show that the metal is present as a single atom, yet they cannot prove that that atom is not combined with a certain number of atoms of mercury.

Two other researches may be mentioned. (1) The rates of diffusion of metals in mercury have been found, and when atomic diffusivities are plotted against atomic weights, two curves are obtained; metals which do not form compounds with mercury have higher diffusivities and lie on one curve, whereas metals which are known to form compounds lie on a second curve with lower diffusivities. It has been suggested that compounds MHg_n are formed in which the attached mercury retards the process of diffusion.

(2) Bornemann and Müller (*Metallurgie*, 1910, **7**, 396) determined the electrical conductivity of liquid sodium amalgams, and obtained a marked discontinuity at a concentration of 33·3 atoms per cent. of sodium, showing the existence of the compound $NaHg_2$ in the liquid condition.

The thermal diagram indicates the existence of at least five other compounds of sodium and mercury, but their existence in the liquid condition was not made manifest by the electrical conductivity experiments.

We are led to inquire why this is so. Bornemann and Müller's experiments were carried out at very high temperatures, and it is possible that all the other intermetallic compounds were dissociated; the compound $NaHg_2$ was stable, since it has a much higher melting point, namely, 360°, than the other compounds; this is at the maximum point on the thermal diagram; other compounds, with the possible exception of Na_3Hg, do not show maxima.

It was thought that indications of the existence of the other intermetallic sodium mercury compounds might be obtained if physical properties were investigated at temperatures not far removed from the melting points of the alloys.

The specific volumes of liquid alloys at 110°, 184°, and 237° have already been determined.

The concentration-volume diagram for 110° is shown in Fig. 2.

It is seen that the specific volume of the liquid alloys is a ____
function of the concentration when expressed in percentage of
weight.

The absence of discontinuities shows that the intermetallic com-
pound Na₃Hg does not exist at 110°.

A consideration of Fig. 1 shows that the property of volume
does not suffer any profound change when combination takes
place between the metals sodium and mercury, so further investi-

FIG. 2.
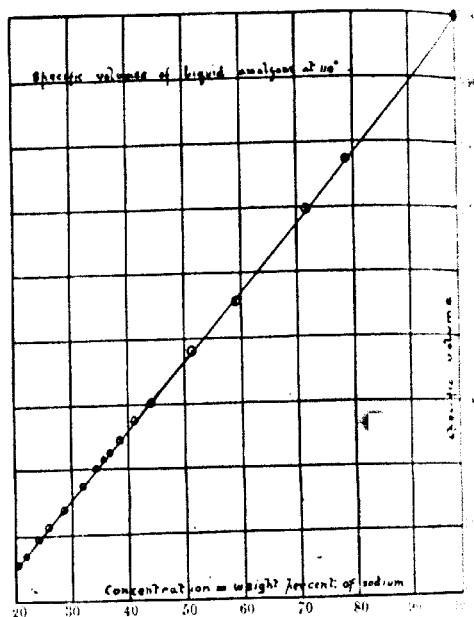
gations were made by means of electrical conductivity measure-
ments of liquid amalgams.

The Electrical Conductivities of Liquid Amalgams

The method of experiment has already been described in a former
paper. The amalgams were kept under paraffin, and drawn
into a capillary spiral having platinum terminals sealed into
glass at convenient points.

The spiral was open at the lower end and fitted with a glass p at the top. It was connected to a hydrogen apparatus, and after allowing any amalgam to enter, it was dried and filled with hydrogen.

The capillary was 1 mm. in diameter, and the distance between platinum terminals about a metre when unwound. It was tested by finding the resistance of mercury filling the spiral.

Fig. 3.
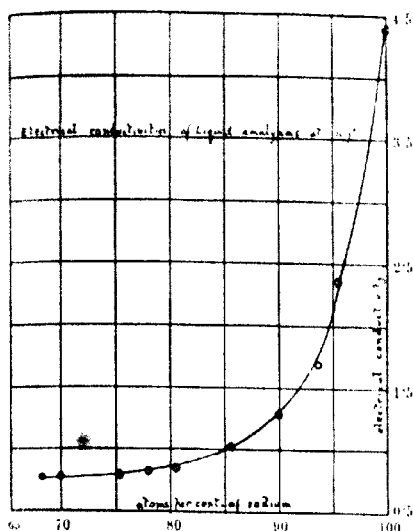
Temperatures of approximately 110° and 135° were obtained by setting with boiling toluene and xylene.

The results are given in the table below; concentrations are given in atomic percentages of sodium; the resistances refer a spiral in which the resistance of mercury at 17° is 1 ohm.

It will be noticed that conductivity measurements have been made for each alloy at two temperatures differing by 26°. The value for the temperature-coefficient has thus been obtained.

Electrical Conductivities of Liquid Amalgams.

Concentration.	Resistance at 107°.	Conductivity.	Resistance (133°).	Conductivity.	Temperature coefficient.
100	0·2285 0·2286 0·2266 0·2260	4·397	0·2455 0·2449 0·2477	4·065	0·0171
95·36	0·4225	2·366	0·4334	2·307	0·0173
93·54	0·5835	1·714	—	—	—
89·88	0·7749	1·2905	0·8139	1·2286	0·0173
85·60	0·9796 ■	1·0208	1·0133	0·9868	0·0176
80·50	1·1569	0·8643	1·1627	0·8600	0·0133
77·89	1·2124	0·8248	1·2248	0·8164	0·0182
75·31	1·2532	0·7979	1·2584	0·7946	0·0171
71·74	—	—	1·3087	0·7641	
70·02	1·2921	0·7739	1·3096	0·7635	0·0169
68·08	1·2968	0·7711	1·3208	0·7571	0·0162

FIG. 4.

Atoms of sodium per 100.
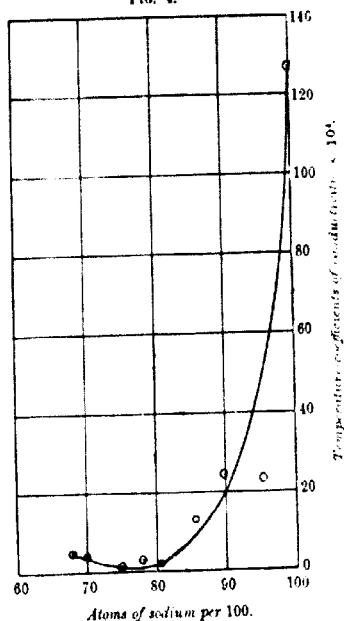
The conductivity-concentration curve for 107° is shown in Fig.
It is a rectangular hyperbola possessing no discontinuity
results for 135° form a similar curve, which would be
below that in Fig. 3.

It will be observed that the fall in conductivity is most marked at 100 to 85 atoms per cent. of sodium, the conductivity at per cent. being less than one-fourth the value for pure sodium. May be pointed out that the concentration of 85 per cent. is of the eutectic point in the thermal diagram.

The differences in conductivity for a temperature range of 26° small, and become much smaller as the mercury content of the ers increases.

The temperature-coefficient falls with extreme rapidity as we from pure sodium to alloys containing 5 and 10 atoms per ut of mercury. The coefficient has an extremely small, almost ssant value for alloys containing more than 20 atoms per cent. mercury. This is shown in Fig. 4. The curve does not give any ication of the formation of compounds.

The conclusion to be drawn from electrical conductivity measure ts for liquid amalgams is thus the same as from specific volume terminations, namely, that the intermetallic compounds of um and mercury are completely dissociated in the liquid dition.

It is possible also from the present and from previous work to pare the relative values of the properties specific volume, trical conductivity, and freezing point in determining the stution of alloys, and it is quite evident that the last is far ur in the certainty of its indications.

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XLVI.—*The System Ethyl Ether Water Potassium Iodide-Mercuric Iodide. Part III. Solutions Unsaturated with Respect to Solid Phases in the Four-component System.*

By ALFRED CHARLES DUNNINGHAM.

fact that the surfaces of saturation with respect to solid phases de the tetrahedron into two parts has been used as an arbitrary sion in the consideration of the system. That part representing rsaturated solutions, or complexes of solid and solution, has ady been considered (this vol., p. 721, *et seq.*). The other sents liquid phases only, and extends from the surfaces of

saturation with respect to solid to the edge BC of the tetrahedron (Fig. 11, Part II). It is therefore bounded by the solid mixture surfaces and portions of the side-planes, namely, $BFGHIZ$ and $Cabefmgde$ on ACD, $BFNMaC$ on ABC, and $BZQPe C$ on B. It has been found experimentally that liquid mixtures unsaturated with solid phases can exist as one, two, or three layers respectively.
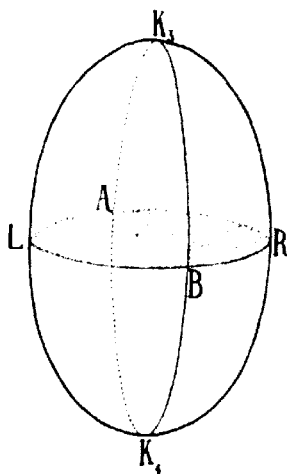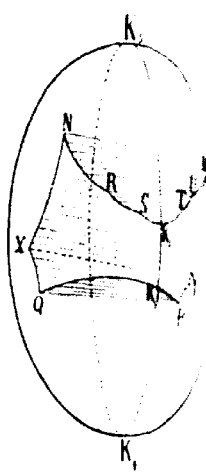
The above space representing liquids only is therefore divided into at least three parts, corresponding with these three cases.

The Formation of Two Liquid Layers.

It will be well to consider first the conditions under which the mixtures, unsaturated with solid phases, can exist as two layers. In a four-component system all such mixtures lie inside what may be called a "two liquid volume," whilst the layers themselves are given by points on the surface enclosing this volume. A "two liquid volume," if complete, is more or less egg-shaped, and encircled by a critical curve, AK_3BK_4, as shown in Fig. 13.* The critical curve divides the binodal surface into two parts, so that any solution a on one part is conjugate with a definite solution

* For Fig. 12, see this vol., p. 731.

the other part. The line ab, which lies entirely inside the two-liquid space, represents all mixtures of a and b.

A "two-liquid volume" may be intersected by the side-planes of the tetrahedron, or by the solid saturation surfaces of the system, so that part of it becomes metastable. In Fig. 13 $LARB$ represents a curve of intersection, so that either the upper or lower part of the two-liquid space is rendered metastable. ALB and RB are conjugate curves, that is, solutions given by points on ALB are in equilibrium with definite solutions given by points on RB. That this must be so will be seen at once from the following considerations. When $LARB$ is the curve of intersection of a side-plane with the binodal surface, it lies entirely in that side-plane, which represents a three-component system. If solutions on ALB are not in equilibrium with solutions on ARB, they would there be conjugate with solutions given by points somewhere else, the right-hand side of the binodal surface; that is, either inside or outside the tetrahedron. In the former case a solution on ALB a three-component system would be in equilibrium with a solution in a four-component system in the latter with a non-existent solution. Neither of these cases is possible. In a similar way it can be shown that when the binodal surface is intersected by a solid saturation surface, ALB and ARB are conjugate, for if they were not, a saturated solution would be in equilibrium with either an unsaturated or a supersaturated solution. When, however, the binodal surface is intersected by a plane such as ALD Fig 11 (Part II), ALB and ARB are not necessarily conjugate. In Fig. 11 (Part II) $NRSK_1TUM$ and QK_2P are curves of inter-section of a binodal surface and the solid saturation surfaces, whilst N and MY, QX and PY are curves of intersection of the binodal surface and the side-planes. $XNRSK_1TUMYPK_2QZ$ therefore represents the boundary of the stable portion of the binodal surface, K_1 and K_2 being points on the critical curve, the stable part of which therefore extends from K_1 to K_2.

The relation between the stable and metastable portions of the two-liquid space is shown in Fig. 14, which is lettered to correspond to Fig. 11. The critical curve K_1K_2 divides the stable portion of the binodal surface into two parts, $NRSK_1K_2QX$ and

$$MUTK_1K_2PY,$$

so that all solutions given by points on one part are conjugate with solutions given by definite points on the other part. When, therefore, all pairs of conjugate points on $NRSK_1K_2QX$ and UTK_1K_2PY are joined, a space is formed, inside which lie all the mixtures existing as two layers. This space is bounded by the stable portion of the binodal surface, $XNRSK_1TUMYPK_2QZ$,

and the surfaces formed by joining all pairs of conjugate points on the following pairs of lines: K_2Q and K_2P, QX and PY MU and YM, NR and MU, RS and UT, SK_1 and TK_1. Outside this space lie unsaturated homogeneous liquids, so that the whole binodal surface divides the unsaturated space into two parts, one of which represents liquid mixtures existing as two layers the homogeneous liquids. The latter is bounded by the two surfaces (see Fig. 11, Part II):

(1) The binodal surface $XNRSK_1TUMYPK_2QZ$.

Fig. 15.
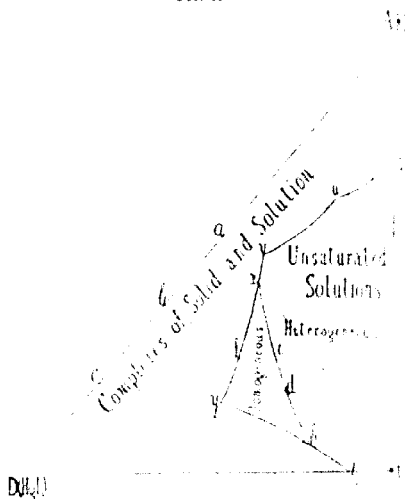
(2) The saturation surfaces $FNRG$, $MabU$, $GRSH$, $Ubcto$ HSK_1TwJ, $ZJwpnmgdePK_2Q$.

(3) The portions of the side-planes $BFGHJZ$ on CB $Cabefmgde$ on ACD, $BFNX$ and $CaMY$ on ABC, and $ZQabe$ $Ouve$ on BDC.

The conjugate curves cp and fn, cd and fg, gn and dp appear to be intersections of saturation surfaces and side-planes with a new binodal volume which extends into the tetrahedron, and, as will be shown later, intersects the binodal volume, of which

$$NRSK_1TUMYPK_2QX$$

is the stable part of the surface.

As in the case of solutions saturated with solid phases, the

occurring in the system are best understood by studying the sections of a series of planes with the binodal and saturation faces. Fig. 15 shows diagrammatically the curves of intersection with a plane as ADL in Fig. 11. As in Fig. 12 (Part II), $xyhk$ is the curve of intersection of the solid saturation surfaces, x and h lying on the critical curves SK_1T and QK_2P respectively. The intersection of the plane with the stable binodal surface therefore extends from x to h, as shown by the curve xdh in Fig. 15. In this figure it is assumed that L represents a mixture of ether and water in which neither component is present in sufficiently large proportion to cause complete miscibility. $qx xyhkL$ represents liquid mixtures. Those lying on $xdhy$ are homogeneous; those $xxxdhkL$ exist as two layers. If L is joined to x and h, and xd Lh are produced to meet AD in a and c respectively, the AD, which represents mixtures of potassium and mercuric iodides, is divided into three parts. Points on Aa and cD represent mixtures which on addition to L cause saturation without homogeneity. Mixtures on ac, however, on addition to L cause the liquid to become homogeneous before saturation is reached; for example, on adding the solid mixture b to the liquid L, the mixture follows the line Lb. From L to d it exists as two layers; at d it becomes homogeneous, and then follows df until saturation is reached at f. The solid phase is necessarily potassium mercuri-iodide, mercuric iodide, or, if Lb passes through y, a mixture of the two.

The position of L on BC (Fig. 11) determines the positions of x and y on the curves SK_1T and QK_2P respectively. In most cases the plane ADL cuts the critical curve K_1K_2 in a point e; xe and eh are on opposite sides of this critical curve. When, therefore, Lb cuts xe, which represents upper or ethereal layers, the mixture becomes homogeneous by the disappearance of the lower layer and persistence of the upper. When it cuts eh (as in Fig. 15), which represents lower or aqueous layers, homogeneity ensues by the disappearance of the upper layer and persistence of the lower. When Lb passes through e, the two layers become identical. The curve xdh can lie entirely on one or other of the binodal surfaces without intersecting the critical curve. When it lies entirely on the part representing upper or ethereal layers, all mixtures become homogeneous by the disappearance of the lower layer; similarly, when it lies entirely on the part representing lower or aqueous layers, all mixtures become homogeneous by the disappearance of the upper layer.

The Formation of Three Liquid Layers.

In a ternary system three liquid layers, unsaturated with respect to solid phases, arise through the intersection of three binodal curves (see Roozeboom, "Die Heterogene Gleichgewichte," Part 2). In a quaternary system the three layers arise through the intersection of three "two-liquid volumes." Fig. 16 shows the simplest case of this, where three liquid layers occur in the two ternary systems ACB and ADB. Thus, in the system ACB, aI_1, bK_1c, cK_2a are the stable portions of three binodal curves intersecting in a, b, and c. These points of intersection represent

Fig. 16.
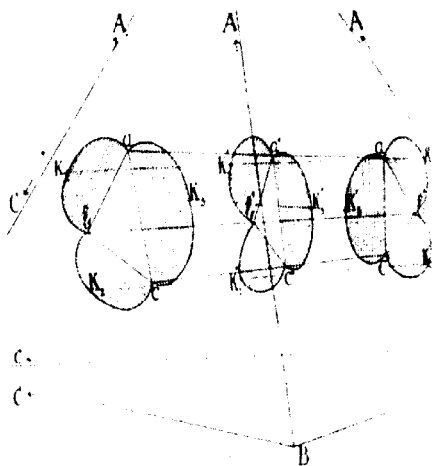
three conjugate liquids, the composition of which cannot vary in a ternary system; similarly, in the system ADB, $a'K_3'b'$, $b'K_1'c'$, $c'K_2'd'$ are the stable portions of the binodal curves, a, b, and c the three conjugate liquids. We have already seen that a binodal curve in a ternary system may be considered as arising from the intersection of the side-plane representing the ternary system with the surface of a "two-liquid volume" in the quaternary system. It therefore follows that between each pair of binodal curves in the ternary systems ACB and ADB a binodal surface extends through the four-component system. There are thus three binodal surfaces intersecting along the lines aa', bb', and cc'. These are

present series of three conjugate liquids, such that a solution represented by a point a'' on the line aa' is in equilibrium with solutions represented by definite points b'' and c'' on the lines bb' and cc' respectively. $a''K_2''c''K_1''b''K_2''$ is a section across the area enclosed by the three binodal surfaces, such that a'', b'', and c'' are conjugate points. $a''K_2''b''$, $b''K_1''c''$, and $c''K_2''a''$ are thus two-liquid areas, whilst $a''b''c''$ is a three-liquid area. Any point in this triangle represents a mixture of the three liquids a'', b'', and c''. The position of the point shows the relative amounts in which they are present.

From the consideration of a series of such sections it is clear that the volume enclosed by the three intersecting surfaces is divided into four parts, namely, three two-liquid volumes and a three-liquid volume, lying inside the others, of which $a''b''c''$ is a section.

In the system under consideration three liquid layers do not

Fig. 17.
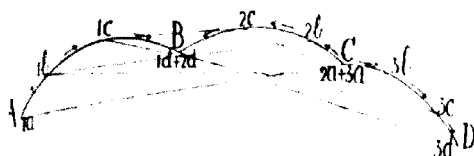
AB *represents bottom layers.*   BC *represents middle layers.*
CD *represents top layers.*

in any of the ternary systems. The three-liquid volume here lies entirely inside the tetrahedron. The three curves representing a series of three conjugate liquids have been determined experimentally, and their form is shown graphically in Fig. 17, the same projection being employed as in Fig. 11 (Part II). The numbers obtained are given in table VI.*

In connexion with the experimental work involved in the three-liquid equilibria, one point is of particular interest. It was found that three stable layers could be obtained easily when freshly purified ether was used, but that ether which has been kept some time, and liberated traces of iodine from the iodide solution, caused a curious form of metastability, which is best illustrated by the following experiments. A liquid mixture was prepared containing 49·243 grams of potassium iodide, 11·067 grams of mercuric iodide, 9·447 grams water, and 19·440 grams of freshly purified ether. This gave three liquid layers which were perfectly stable at 20°. The same mixture, in the preparation of which very "pure" ether was used, gave only two stable layers at 20°. It was found to be possible, however, to prepare three metastable layers by gradually warming the mixture without agitation. Thus, the mixture existed as two stable layers at 10°,

TABLE VI.

The System: Ethyl Ether–Water–Potassium Iodide Mercuric Iodide at 20°.

Three liquid layers with no solid phase

No.	Percentage composition of top layer.				Percentage composition of middle layer.				Percentage ... of bott...		
	KI.	HgI₂.	Et₂O.	H₂O.	KI.	HgI₂.	Et₂O.	H₂O.	KI.	H...	
*57	2·1	6·2	88·3	3·4	16·7	30·8	23·4	29·1	16·7	30··	··
†58	2·2	6·2	87·9	3·7	16·6	30·9	23·2	29·3	–	–	
59	2·2	6·8	87·0	4·0	15·8	30·6	28·5	25·1	18·5	3··	
†60	2·3	6·8	86·7	4·2	14·3	29·4	33·3	23·0	—		
‡61	—	—	—	—	13·2	30·1	37·7	19·0	20·3	33·0	
62	2·7	7·7	85·4	4·2	13·1	28·7	38·7	19·5	20·5	32·0	
63	2·7	7·5	85·4	4·4	12·5	28·8	39·4	19·3	20·8	32·6	
64	4·1	12·8	77·5	5·6	10·3	26·6	47·7	15·4	21·0	34·2	
65	4·5	11·2	78·2	6·1	10·3	25·9	49·1	14·7	22·2	34·5	
66	5·8	16·6	68·9	8·7	8·8	21·9	58·0	11·3	22·4	35·9	
67	6·0	16·8	69·2	8·0	8·7	21·6	58·6	11·1	23·0	34·7	
§68	7·1	19·2	64·3	9·4	7·1	19·2	64·3	9·1	22·4	35·2	

* In No. 57, the middle and bottom layers are identical, that is the critical solution.

† Nos. 58 and 60 give the solutions left when the bottom layer has disappeared.

‡ No. 61 gives the solutions left when the top layer just disappears.

§ In No. 68, the top and middle layers are identical, that is, the critical solution.

Any solution represented by a point on AB is equilibrium solutions represented by points on BC and CD respectively represents bottom, BC middle, and CD top layers. One

but gave rise to three layers when placed in the thermostat without agitation. On shaking, however, the three layers, which were cloudy ....
immediately gave only two stable layers. It was further found that ....
amounts of the three metastable layers depended on the amount .... temperature was raised without agitation. The same phenomena was observed whenever a three-liquid mixture was prepared with ether which had been freshly purified.

It has not been found possible to investigate the matter further, and the nature of the action of impure ether on the equilibrium existing between the layers is still in doubt.   The effects observed, however, were ....
traces of impurity amounting to an almost negligible percentage of the mixture, and it appears probable that these traces of impurity affected the tension existing between two of the layers (the upper two in all cases) .... to such an extent as to render equilibrium between them impossible.

The ether used in the determinations was purified as follows: It was washed with dilute permanganate solution, slightly acidified with sulphuric acid, ... permanganate was no longer decolorised. It was then distilled and left over anhydrous sodium carbonate for some days, when it was again distilled; a third distillation over anhydrous sodium carbonate completed the purification; the final product never produced metastability between three liquid layers.

sions are lettered alike ; thus 1b, 2b, and 3b are in equilibrium a one another. A and C represent two conjugate liquids, such a when A (the lower layer) moves along AB, C (the upper layer) as rise to two layers, which move along CB and CD respectively, as dicated by the arrows. When the top layer (No. 3) reaches B,

FIG. 18.
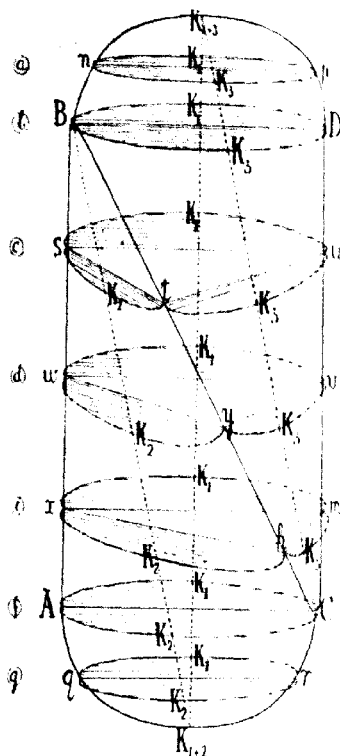
atom (No. 1) and middle (No. 2) layers both reach B, where become identical, thus leaving only two layers, B and D, in .rium. This reaction is reversible. Starting with B and D, D, the upper layer, moves along DC, B, the lower layer, gives o two layers which move along BA and BC respectively.

When the bottom layer (No. 1) reaches A, the middle (No.?), top (No. 3) layers reach C, and become identical, leaving A and C in equilibrium. The changes may be represented thus:

$$L_A + L_C \rightarrow L_1 + \underbrace{L_2 + L_3}_{C} \rightarrow \underbrace{L_1 + L_2}_{B} + L_3 \rightarrow L_1 + L$$

and

$$L_E + L_D \rightarrow \underbrace{L_1 + L_2}_{B} + L_3 \rightarrow L_1 + \underbrace{L_2 + L_3}_{C} \rightarrow L_1 + L$$
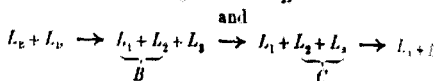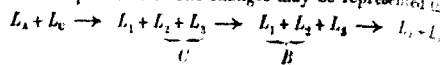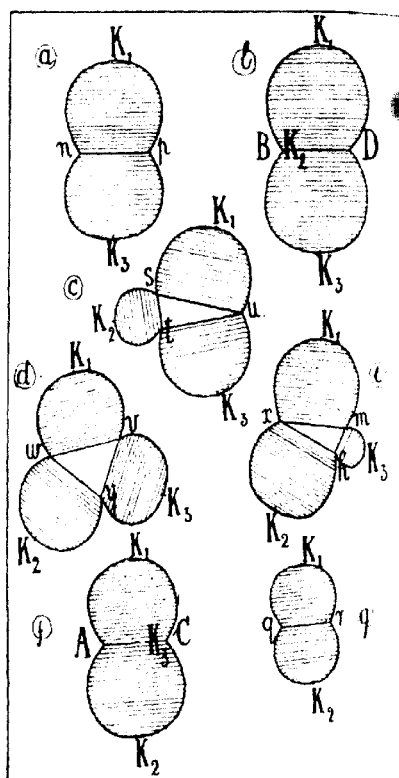
FIG. 19

Fig. 18 shows a type of equilibrium in which the intersec? three binodal surfaces gives rise to three-liquid curves simi?

shown in Fig. 17. The three surfaces, the critical curves of
are lettered K_1, K_2, and K_3 respectively, intersect along AB,
and CD, which are lettered to correspond with Fig. 17. The
diagram is best understood by studying a series of sections
of the figure, which are shown in detail in Figs. 19a, 19b, 19c,
19e, 19f, and 19g. With regard to these, the following points

FIG. 20.
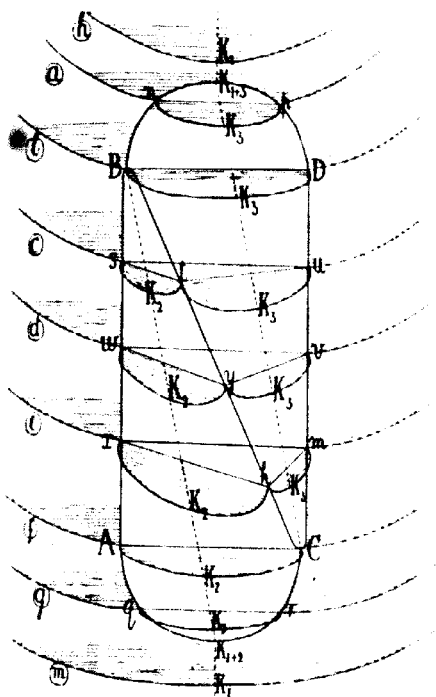
mentioned. In Fig. 18 $BK_{1+2}D$ is the curve of intersection
of binodal surfaces, the critical curves of which meet at K_{1+2}.
This is a section of the space enclosed by these two surfaces.
A point on nK_1pK_3 represents a mixture of two conjugate
Points on nK_1p represent mixtures of liquids on nK_1 and
respectively, lying on binodal surface 1, whilst those on nK_3p
represent mixtures of liquids on nK_3 and pK_3 respectively, lying

on binodal surface 3. Section (*b*) differs from (*a*) in that *t* and
critical solution, from which arise liquids *s* and *t* of ...
Sections *c*, *d*, and *e* show three-liquid areas, namely, *st*...
rhm respectively. In section (*f*) C is a critical solu...

Fig. 21.
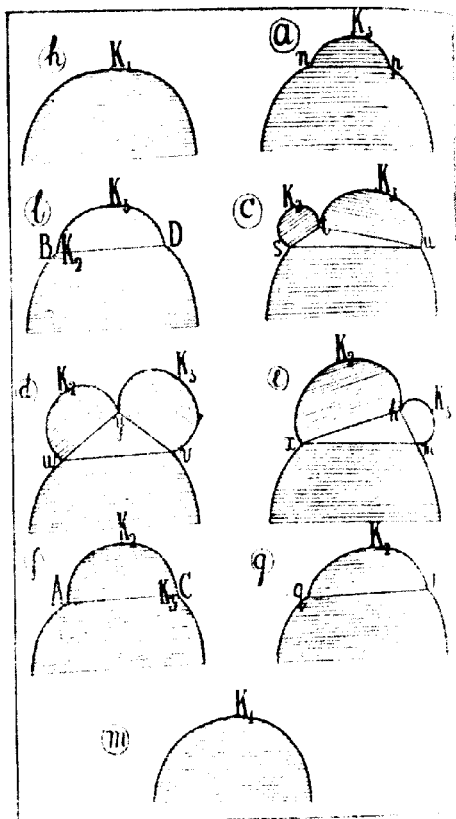
from *w* and *h* of (*e*), which have become identical. (*m*) is ...
as (*a*), with the difference that binodal surface 3 has been ...
by binodal surface 2. The three-liquid volume terminates in ...
lines *BD* and *AC*, and its general form is clear from ...
(*d*), and (*e*).

In the system under consideration two of the intersecting "two-liquid volumes" are also intersected by side-planes of the tetrahedron or by solid saturation surfaces. The curves formed by these intersections have already been considered. There is no indication that the third "two-liquid volume" intersects either side-planes or solid saturation surfaces. Figs. 20 and 21 show modifications of Figs. 18 and 19, which agree more closely with the facts as mentioned. Only a portion of binodal surface 1 is shown, this corresponding with the surface $XNRSK_1TUMYPK_2Q$ of Figs. 11 and 14. The critical curve of this surface, lettered K_1, terminates at the points K_1 and K_2 of Fig. 11. One of the other surfaces

Fig. 22.
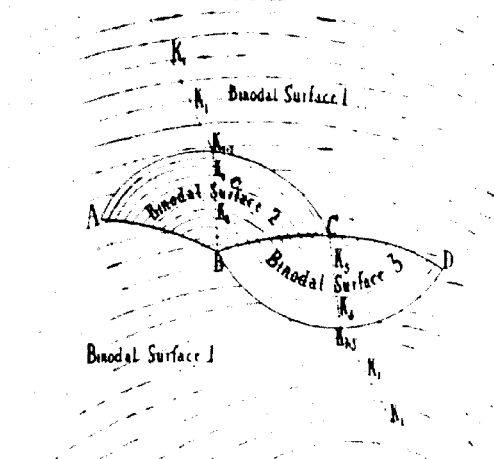
rise to the curves cpd and fng of Fig. 11, which show that the curve is not intersected across its critical curve. These intersections are not shown in Figs. 20 and 21, the significance of which is readily understood by reference to Figs. 18 and 19, to which they bear a close resemblance.

Fig. 22 shows the three binodal surfaces in positions which give rise to curves of intersection having the same relative positions as those of Fig. 17, and since it represents the actual equilibrium as nearly it will be well to consider it in some detail. The letters correspond with those of the preceding figures, AB, BC, and CD again representing the three curves of conjugate liquids. Surface 1, of which part only is shown, corresponds with

$$XNRSK_1TUMYPK_2Q$$

of Figs. 11 and 14, and can be considered as lying in the plane of the paper. The stable portions of the two binodal surfaces intersecting it are shown by $AK_{1+2}CB$ (No. 2) and $BCDK_{1+3}$ (No. 1). AB is the curve of intersection of surfaces 1 and 2, BC that of surfaces 2 and 3, CD that of surfaces 3 and 1. AB and CD therefore lie on surface 1, that is, in the plane of the paper, which only touches it at its end-points, B and C. $AK_{1+2}C$ is the curve along which only surfaces 1 and 2 intersect, $BK_{1+3}D$ that along which only surfaces 1 and 3 intersect. They therefore lie on surface 1, and are both critical curves.

The parts into which the space enclosed by the binodal surfaces is divided are four in number, as follows:

(1) The two-liquid space representing mixtures of two conjugate liquids lying on surface 1. This is bounded by the binodal surface itself, and the surface $ABCD$, formed by joining all pairs of conjugate points on AB and DC. It has already been defined as the space formed by joining all pairs of conjugate points on the binodal surface.

(2) The two-liquid space representing mixtures of two conjugate liquids lying on surface 2. This is bounded by the binodal surface itself, $ABCK_{1+2}$, the surface $AK_{1+2}C$ formed by joining all pairs of conjugate points on AK_{1+2} and CK_{1+2}, and the surface AB formed by joining all pairs of conjugate points on AB and C. The space is thus formed by joining all pairs of conjugate points on the binodal surface.

(3) The two-liquid space representing mixtures of two conjugate liquids lying on surface 3. This again is formed by joining pairs of conjugate points on the binodal surface. It is bounded by the binodal surface itself, together with the surface BK, formed by joining all pairs of conjugate points on BK_{1+3} and DK_{1+3}, and the surface BCD formed by joining all pairs of conjugate points on BC and DC.

(4) The three-liquid space, representing mixtures of three conjugate liquids lying on AB, BC, and CD respectively. It is bounded by the surface $ABCD$, formed by joining all pairs of conjugate points on AB and DC; the surface BCD formed by joining all pairs of conjugate points on BC and DC; and the surface ABC, formed by joining all pairs of conjugate points on AB and CB. The three-liquid space thus lies inside the surfaces formed by joining all sets of conjugate points on AB, BC, CD.

A consideration of Fig. 22 shows that the triangular planes formed by joining three conjugate points on AB, BC, and CD respectively are not parallel to one another. If a plane is drawn

as to intersect the three-liquid space, it may cut the three conjugate curves in points which are either conjugate or not conjugate with one another. The intersecting planes to be considered are those representing mixtures in which ether and water bear a constant ratio to one another, such as ADL in Fig. 11, and those which are parallel to one side of the tetrahedron, representing mixtures of a constant percentage of one particular component.

Fig. 23 is a section formed by a plane such as ADL in Fig. 11, passing through the three-liquid space and across the three conju-

Fig. 23.
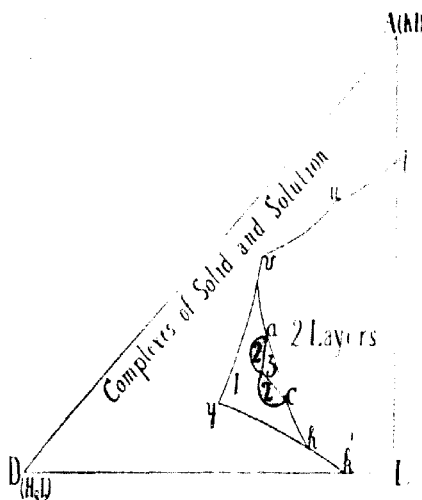
the curves at a, b, and c respectively. The section of the three-fold space is shown on a larger scale in Fig. 24.

We will first consider the case in which a, b, and c are conjugate with one another.   The significance of the areas into which ADK_2G is divided will be clear from what has already been said with regard to the sections in Figs. 19 and 21. When a definite mixture of the two solid components is added little by little to the liquid mixture L, the mixture so formed follows a straight line on the plane ADL, such as $rxqv$ in Fig. 24. As it moves along rv the two layers into which it separates follow Ra and Gc respectively, so that when the mixture is represented by x the layers are represented by a and c. When the mixture moves from x along

vs it enters the three-liquid area, and a third liquid, *c*, ⟨…⟩
separate, *a* and *c* remaining unchanged in composition. A⟨…⟩
approached *b* increases in amount, whilst *c* decreases ⟨…⟩
layer *c* entirely disappears, leaving *a* and *b*. As the m⟨…⟩
follows *sy*, the two layers follow aK_2 and bK_2 respe⟨…⟩
only solution *y* is left, the other quite disappearing. Th⟨…⟩
geneous liquid then follows *yw*, eventually, of cours⟨…⟩
saturated. It is obvious that either the layer on aK⟨…⟩
bK_2 can disappear, or they can become identical, accor⟨…⟩
position of the point *y*, at which *rrsyw* cuts the curve aK⟨…⟩
the mixture follows the line *efghk* the phenomena occurr⟨…⟩

FIG. 24.

similar. Of the three-liquid layers, *a*, *b*, and *c*, howev⟨…⟩
pears, leaving only *b* and *c* when the mixture reaches ⟨…⟩

When the mixture follows a line such as *pmbq*, passi⟨…⟩
b, a slightly different behaviour occurs. At *m*, *a* and *c* r⟨…⟩
the two layers, and as the mixture follows *mb*, the thir⟨…⟩
separates, and increases in amount whilst *a* and *c* decr⟨…⟩
b, *a* and *c* disappear simultaneously, leaving only *b*, wh⟨…⟩
traverses the homogeneous area along the line *bq*.

When the plane intersects the three-liquid space in ⟨…⟩
that *a*, *b*, and *c* are not conjugate points, the section ⟨…⟩
similar in form to that shown in Fig. 24, is no longer ⟨…⟩
quantitative interpretation. Thus, a point inside the ⟨…⟩
abc represents a mixture of three layers, but these are ⟨…⟩

... by the points a, b, and c. The plane cuts across a number ... triangles, so that as the mixture follows the line ... the three layers change, not only in amount, but in composi... Similarly, the compositions of the layers composing mixtures ... two-liquid areas are not given by points on the bounding

... plane can intersect the three-liquid space in a variety of ways, ... rise to various special forms of sectional curves, such as those ... when the plane intersects the three-liquid space without ... all three conjugate curves (AB, BC, and CD). The forms ... various sections can be readily determined, and will not ... considered here.

... author desires to acknowledge a grant from the Chemical ... towards the expenses of this research.

SIR JOHN DEANE'S GRAMMAR SCHOOL.
NORTHWICH, CHESHIRE.

XXVII.—Resolution of trans-cycloPentane 1 : 2-dicarboxylic Acid.

By LEONARD JAMES GOLDSWORTHY and WILLIAM HENRY PERKIN, jun.

... accordance with the theory of Le Bel and van't Hoff, many ... dicarboxylic acids of the cyclic hydrocarbons should be ... of resolution into optically active modifications. Hitherto, ... two acids of this type have been investigated in this respect, ... first to be resolved was trans-hexahydrophthalic acid:

$$CO_2H \quad H$$

$$CH_2 \cdot CH_2 \cdot C$$
$$CH_2 \cdot CH_2 \cdot C$$

$$H \quad CO_2H$$
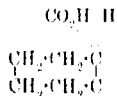
... 1899, Werner and Conrad (Ber., **32**, 3046) showed that this ... totally compensated acid may be resolved into its active ... modifications by the fractional crystallisation of the quinine salts. ... the active acids were found to have $\alpha_D + 18.2°$ and $- 18.5°$ ... respectively. These investigators also showed that, whilst the ex... nally compensated acid is almost insoluble in water and melts

at 215°, the d- and l-modifications melt at 179--183°, ...
much more soluble; again, the anhydrides of the active ...
at 164°, or considerably higher than that of the dl-acid ...
melts at 140°. Furthermore, the conversion of the acids ...
their anhydrides is attended by a reversal and at the same ...
considerable increase of the rotation, since the d-acid ...
yields an anhydride with a_D $-76.7°$; the dimethyl esters ...
same sign as their acids and the rotations a_D $+28.6°$ ...
respectively. At a later date (*Brr.*, 1905, **38**, 311) ...
and von der Heide investigated *trans-cyclo*propane ...
oxylic acid,

$$CH_2<^{CH \cdot CO_2H}_{CH \cdot CO_2H}$$
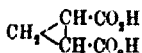
and showed that this acid can be resolved into its active ...
ponents by the fractional crystallisation of the salts with ...
quinine, or cinchonidine. The active acids melt at 175°, ...
at the same temperature as the dl-acid, and have a_D ...
attempts to prepare the anhydrides of these acids have ...
successful, since they distil unchanged and are not acted ...
acetyl chloride.

Some years ago, a series of experiments was commenced ...
the Laboratories of Manchester University by one of us ...
junction with Mr. H. D. Gardner with the object of ...
the resolution of *trans-cyclo*pentane-1:2-dicarboxylic acid.

$$CH_2<^{CH_2 \cdot CH \cdot CO_2H}_{CH_2 \cdot CH \cdot CO_2H}$$

(Perkin, T., 1887, **51**, 244), but the investigation ...
completed.

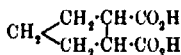We have now taken up the subject again and find that res...
may be readily and completely brought about with the ...
brucine.

When the dl-acid is combined with brucine and the ...
are recrystallised from water, the salt of the d-acid separates ...
and is readily obtained pure by repeated recrystallisation ...
l-acid may then be recovered from the mother liquors ...
manner described on p. 2643. The observed rotations of the ...
l-modifications were a_D $+87.6$ and -85.9 respectively, and ...
of the corresponding ethyl esters, a_D $+70.31°$ and ...
d- and l-modifications of *cyclo*pentane-1:2-dicarboxylic ...
at 181° or 21° higher than the melting point of the dl-...
tion (m. p. 160°). For the sake of ready comparison, the ...
and melting points of the *trans-cyclo*propane-, pentane-...
-hexane-1:2-dicarboxylic acids are appended in tabular for...

	a_D d-acid.	a_D l-acid.	M. p. of d- and l- acids.	M. p. of inactive acid.
*cyclo*Propane- 1 : 2-dicarboxylic acid	+ 84·9°	84·5	175°	175°
*cyclo*Pentane- 1 : 2-dicarboxylic acid	+ 87·6	85·9	181°	160°
*cyclo*Hexane- 1 : 2-dicarboxylic acid	+ 18·2°	− 18·5	178—183°	215°

would be interesting to fill up the gap between *trans-cyclo*-
pane-1 : 2-dicarboxylic acid and the corresponding *cyclo*pentane-
carboxylic acid by the resolution of *trans-cyclo*butane-1 : 2-di-
carboxylic acid,

$$CH_2 \cdot CH \cdot CO_2H$$
$$CH_2 \cdot CH \cdot CO_2H$$
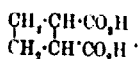
unfortunately, the preparation of this acid (T., 1894, **65**, 585)
quantity sufficient for resolution is most troublesome and,
rough experiments with this object have been commenced, we
not yet been able to separate the active modifications in a
state.

EXPERIMENTAL.

d-trans-cyclo*Pentane*-1 : 2-dicarboxylic Acid.

The dl-*trans-cyclo*pentane-1 : 2-dicarboxylic acid employed in
experiments was prepared by the method described by Perkin
(1887, **51**, 240; compare T., 1894, **75**, 586). The pure acid,
quantities of 15 grams, dissolved in hot water, was mechanically
stirred and brucine (90 grams) gradually added, when the alkaloid
soon dissolved. The excess of brucine was filtered off, well
washed with hot water, and the filtrate and washings were con-
centrated on the water-bath until crystals just commenced to form
on the surface. When the liquid was cooled and vigorously stirred,
copious crystallisation took place, and the whole became semi-
solid, the crystals were then collected and repeatedly recrystallised
from hot water. During this operation, the progress of the separa-
tion of the brucine salt of the d-acid from that of the l-modifi-
cation was followed with the polarimeter, and the table given
below shows that the separation is nearly complete after six crys-
tallisations, since the difference between the rotation of this crop
and that obtained as the result of the twelfth crystallisation
very small.

No. of crystallisation.	Weight of substance. Gram.	Observed rotation.	Specific rotation.
1st crop	0·5250	− 1·68°	− 32·1°
3rd ,,	0·4566	− 1·14°	− 25·0°
6th ,,	0·5050	− 1·15°	− 22·8°
12th ,,	0·2612	− 0·51°	− 19·9°

A specimen of the pure brucine salt was subsequently prepared
by adding excess of brucine to the hot dilute aqueous solution of
the pure *d*-acid (see below), and, after filtering, the solution was
allowed to crystallise slowly over sulphuric acid, when small,
brilliant, tabular crystals separated. As these crystals effloresce
in a vacuum desiccator, they were dried by exposure to air and
then analysed:

0·1314 gave 0·2782 CO₂ and 0·0859 H₂O. C = 57·7; H = 7·3
0·5079 .. 22·6 c.c. N₂ at 19·8° and 753 mm. N = 5·1
2C₂₃H₂₆O₄N₂·C₇H₆O₄·9H₂O requires C = 57·4; H = 7·1; N

per cent.

That the salt has this composition was confirmed by the fact
that 0·2316 gram, heated for one hour at 125°, lost 0·0336 gram,
whereas the calculated loss for 9H₂O is 0·0339 gram.

In order to obtain the pure *d*-acid, the brucine salt from the
twelfth crystallisation was dissolved in hot water, the base
precipitated by ammonia and, after filtering and washing, the
solution of the ammonium salt was concentrated and acidified
with hydrochloric acid when, on cooling, the *d*-acid separated
in plates, and melted at 178—180°. After completely drying
with the aid of animal charcoal, and twice crystallised from
water, the acid melted at 181°, and 0·1752 dissolved in water
(20 c.c.) gave, in a 2 dcm. tube, a rotation of +1·53°, whence
a₀ +87·6°. On titration, 0·1778 required 0·0899 N·NaOH for
neutralisation, whereas this amount of an acid, C₇H₆O₄, O₃
should neutralise 0·0900 NaOH.

The d-*ethyl ester*, C₇H₄(CO₂Et)₂, was prepared by heating the
d-acid with five times its weight of 10 per cent. alcoholic sulphuric
acid for six hours; water was then added, the ester extracted with
ether, and, after washing with water and dilute sodium carbonate,
the ethereal solution was dried, evaporated, and the ester distilled
under diminished pressure.

It boiled constantly at 170°/100 mm., and 0·2596, dissolved in
acetone (20 c.c.), gave, in a 2-dcm. tube, a rotation of +3·1°,
whence **a**₀ +70·31°.

The d-Anilide, C₇H₄(CO·NH·C₆H₅)₂. In order to prepare this
derivative, the *d*-acid was heated with thionyl chloride in a sealed
tube in boiling water for an hour, the clear liquid evaporated on
the water-bath, and the residual acid chloride dissolved in benzene
and mixed with excess of aniline. The benzene was removed by
evaporation, the residue stirred with dilute hydrochloric acid,
the crystalline precipitate collected and recrystallised twice from

methyl alcohol, in which it is sparingly soluble, separating as a gelatinous mass of needles melting at 245°–247° (uncorr.):

0.2756 gave 21.7 c.c. N_2 at 18.4° and 762 mm. N = 9.1.

$C_{19}H_{20}O_4N_2$ requires N = 9.1 per cent.

This, dissolved in acetone (20 c.c.), gave, in a 2-dcm. tube, a rotation +1.880°, whence $\alpha_D = +110.1°$.

Attempts which were made with the object of preparing the anhydride of the *d-trans* acid were not successful and the results obtained seem to throw some doubt on the existence of this anhydride. Since, however, *trans*-cyclohexane-1 : 2-dicarboxylic acid (*cis*-hexahydrophthalic acid) yields an anhydride without difficulty (Baeyer, *Annalen*, 1890, **258**, 179), there is every reason to suppose that the anhydride of *trans*-cyclopentane-1 : 2-dicarboxylic acid should also be capable of existence, but it is doubtful whether the substance described by Haworth and Perkin (T., 1894, § 986) can be accepted as this anhydride.

l-trans-cycloPentane-1 : 2-dicarboxylic Acid.

In order to obtain this acid, the mother liquors from the first crystallisations of the brucine salt of the *dl* acid (p. 2641) were concentrated until crystals began to appear on the surface of the hot liquid. The salt, which separated in quantity on cooling, is dissolved in hot water, the solution decolorised with animal charcoal, and the crude *l* acid isolated in the manner described in the case of the *d*-acid.

The acid is readily obtained pure simply by recrystallising four times from water, it then melted sharply at 180°–181°, and 0.2363, dissolved in water (20 c.c.), gave, in a 2-dcm. tube, a rotation of −1.3°, whence $\alpha_D = −85.9°$. On titration, 0.3110 required 0.1568 NaOH for neutralisation, whereas this amount of an acid, $C_7H_{10}O_4$, should neutralise 0.1575 NaOH.

The ethyl ester, $C_5H_8(CO_2Et)_2$, obtained in the manner described in detail in the case of the ester of the *d*-acid, distilled at 161°–162° mm., and 0.3326, dissolved in acetone (20 c.c.), gave, in a 2-dcm. tube, a rotation of −2.32°, whence $\alpha_D = −69.76°$.

THE UNIVERSITY MUSEUM,
    OXFORD.

CCXLVIII.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part IX. The Rotatory Powers of* l-*Naphthyl-methyl-carbinol and its Esters.*

By JOSEPH KENYON and ROBERT HOWSON PICKARD

THIRTY EIGHT optically active carbinols of the formula

$$R_1 \cdot CH(OH) \cdot R_2$$
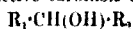
have been described so far in this series of investigations, and with one exception have been shown to possess certain characteristics as regards dispersive power. Thus their rotatory powers for light of wave-length ranging from that of sodium yellow to that of mercury violet not only increase continuously with decreasing wave-length (that is, the compounds exhibit what is commonly spoken of as normal dispersive power), but also conform to the law of simple dispersion expressed by Drude's equation with one term, $a = k/\lambda^2 - \lambda_0^2$ (compare Lowry, Pickard, and Kenyon, this vol., p. 94). Further, a dispersion ratio, such as, for example, Hg_{green}^{violet}, is in the cases of many of the carbinols approximately constant over a range of temperature extending up to their boiling points, and even in the others varies only to a very slight extent, whilst the dispersion ratio is only affected to a very slight extent by solvents. It is probable, however, that this is a special property of this class of compounds, the rotatory powers of which are not affected to any large extent by increase of temperature or solvent. Indeed, on reference to the " characteristic diagrams " (for example, see Part V., this vol., p. 847) for a homologous series of the carbinols these properties appear as an obvious arithmetical fact, since the violet and green lines of the diagrams intersect so as to the zero. It should, however, be borne in mind that the method of plotting rotation data known as "characteristic diagrams" as developed by the present authors for the correlation of the rotation data of many compounds of allied structure—whilst great extremely useful in several directions—is, however, largely empirical, having been devised originally on theoretical grounds by Armstrong and Walker (*Proc. Roy. Soc.*, 1913, [A], **88**, 388) to aid in the explanation of the *anomalous* dispersion of a compound by assuming the presence in it of two dynamic isomerides of different optical properties.

It also seems desirable to suggest that inferences drawn from

...tions in the magnitude of a dispersion ratio are likely to prove ...ding, whilst the use of negative and positive signs for such ...in the region of what is commonly known as anomalous ...sion has apparently no meaning whatever.

Among the carbinols referred to above the conspicuous excep... is βl-naphthylmethylcarbinol (Part VI., this vol., p. 1116). The rotations of this compound appear to obey the law of simple dispersion only at temperatures above 160°, whilst in the super-...ed state the carbinol exhibits the phenomenon known as anoma-...us dispersion at and below a temperature of about 10°. So extraordinary, then, are the optical properties of this carbinol that ...ened desirable to investigate some of its homologues, but owing to the many experimental difficulties only dl-naphthyl-n-hexyl-...rbinol has been prepared.

The properties of the new carbinol are quite analogous to those of the corresponding methyl compound. Thus in the homogeneous state (see Fig. 1 and table I) the dispersion is "anomalous" (for ...ow to violet light) at temperatures between about 22° and 38°, ...t the rotations conform to the law of simple dispersion at about ...d above a temperature of 180°. The regular character of the ...ation curves seems to negative any suggestion that the anoma-...s dispersion is due specially to polymerisation in the neighbour-... of the melting point of the carbinol, although they show that ... cause of the "anomaly" is gradually removed by increase of ...perature

The majority of chemists appear to favour the explanation of ...alous dispersion in compounds of simple constitution by the ...mption of the presence in what is otherwise the homogeneous ...pound of two dynamic isomerides differing in optical sign and ...tative power. It has been suggested already (Part VI., loc. cit.) ... in the case of these naphthylcarbinols such isomerides are ...ed by a difference in the disposition of the valencies in the ...thyl radicle. An alternative suggestion made by Patterson ...913, 103, 145) that this phenomenon is due to a succession ...axima and minima on the rotation curves occurring at different ...peratures for light of various refrangibilities, whilst very diffi-... of direct experimental test, is nevertheless rendered very ...ful in the authors' opinion by the accumulation of data ...ced in these investigations.

... has now been shown that the presence in an optically active ...pound of a naphthyl group attached at the "α"-position or ... esterified carboxylic group is associated very frequently with ...henomenon of anomalous dispersion. In each case tempera-

VOL. CV.   8 K

ture has a great effect on the phenomenon, increase of temperature
destroying it in the case of naphthyl compounds, but bringing it
to view in the case of the esters. It is desirable, however, that the
term "anomalous" dispersion should no longer be used. Perhaps

FIG. 1.

Temperature.
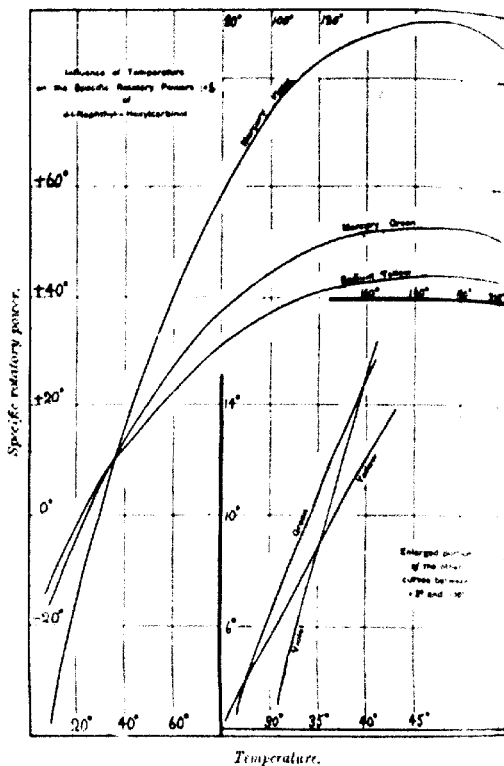
of the rotation curves on either side of the region of "anomalous"
dispersion have dispersion ratios which rapidly increase or decrease
"Anomalous" dispersion as commonly understood refers as a rule
merely to portions of the rotation curves artificially selected according
ing to the wave-lengths of light under consideration. In very

Lowry's work (T., 1913, **103**, 1067 *et seq.*) it is much better to use only the terms *simple* and *complex* as applied to dispersive power according as the rotations conform to Drude's equation with one or more terms.

Among the large number of compounds studied in these investigations the l-naphthylcarbinols at low temperatures and the esters described in the authors' previous communications at high temperatures tend, then, to exhibit *complex* dispersive power, the dispersive power becoming *simple* in each case if the conditions of temperature are reversed.

These generalisations * are confirmed by the optical properties of the esters of the two naphthyl carbinols with normal fatty acids, since it has been found that the acetate of *l*-1-naphthylmethyl-carbinol and a homologous series of esters (ranging from the acetate to the *n*-undecoate) of *d*-1-naphthyl-*n*-hexylcarbinol each exhibits complex dispersive power at all temperatures from 20° to 200°, the limits of the experimental conditions. The dispersion ratios for these esters are not affected much by temperature, and are nearly identical throughout the series. This is noteworthy, not only for the exceptions, but also as occurring in a series all members of which have complex dispersions. The dispersion ratios of each ester, however, are about 5 per cent. greater in carbon disulphide solutions than in the homogeneous state.

The configurations ascribed to *l*-1-naphthylmethylcarbinol and *l*-naphthyl-*n*-hexylcarbinol, although these compounds and some of their derivatives are under certain conditions dextro- and lævo-rotatory respectively, are justified by drawing the characteristic diagram for each carbinol, when it will be found that the two diagrams form exact mirror images of one another. As has been already mentioned, such diagrams are based on the assumption of the presence in the carbinols of two dynamic isomerides differing in optical sign and dispersive power, but in the case of the esters of these carbinols there may be assumed to be present four dynamic isomerides in each ester. It is therefore not surprising that the rotation data for the esters recorded in the experimental part cannot be correlated on the characteristic diagrams of the carbinols, although these four dynamic isomerides would in pairs have the same optical sign.

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* The authors are aware that many of the generalisations stated in this and the other papers of the series are open to the criticism that the same are based on rotatoric readings of small magnitude. However, they feel that the concordant results which have now been obtained for a very large number of compounds justify these generalisations.

The trend of the values of the molecular rotatory power of the members of this series of esters is dissimilar to those of the other

FIG. 2.

Number of carbon atoms in acyl group.
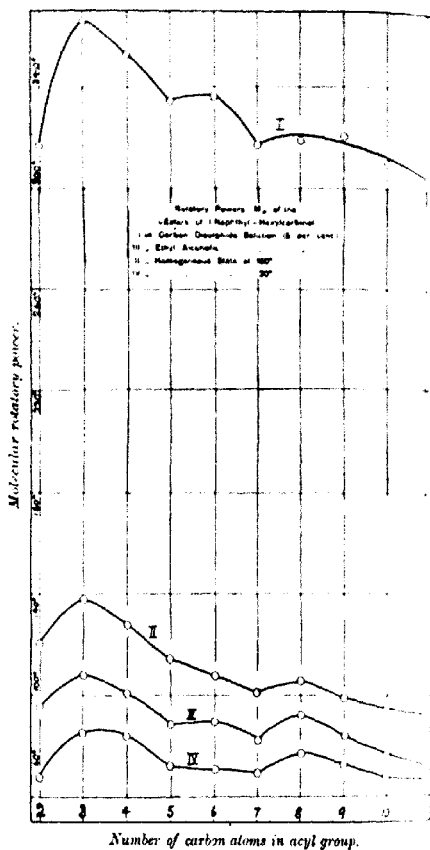
series of esters described in these investigations. Thus it will be seen from Fig. 2 that the curves connecting molecular weight and molecular rotatory power determined under several conditions (

temperature and solution show maxima at the propionate and valerate in addition to the maximum so commonly exhibited at the

Fig. 3.

valerate (or valerate). This somewhat irregular result is perhaps as surprising in a series of esters of such complexity, that is, as compared to the esters previously described, which have been those

of carbinols of simple structure (compare, however, Part III
1912, **101**, 1430). To explain this is difficult, but it is signifying
that the maxima at the propionate and octoate follow one another
at points in the series in the interval between which the chain has
grown by five carbon atoms, that is to say, at the octoate the
growing chain may be assumed to have all but returned to the
position occupied by it in the propionate. It is, however, possible
that the mass of the growing chain as it approaches (or just exceeds)
that of one of the other groups (for example, the hexyl or naphthyl
group) may have an additional effect on the molecular rotatory
power and cause some special exaltation.

In Fig. 3 the effect of temperature on the rotatory powers of the
esters is illustrated. In general this effect (within the experimental
limits) is a common one on all the members of the series, although
there is a significant change of slope in the curve for the octoate

TABLE I.

d-1-Naphthyl-n-hexylcarbinol.

Temperature.	D_4^t.	$[\alpha]_{D}^t$.	$[\alpha]_{\alpha'}^t$.	$[\alpha]_{H}^t$.	$[M]_{D}^t$.	$[M]_{\alpha'}^t$.	$[M]_{H}^t$.	$[\alpha]_{H}^t$
10°	1·0310	−11·26°	−14·89°	−40·25°	−27·24°	−36·03°	−97·40°	?
20	1·0232	−1·51	−2·05	−12·75	−3·66	−4·97	−30·85	?
40	1·0075	+12·46	+13·85	+16·92	+30·15	+33·52	+40·96	?
60	0·9911	23·29	26·89	40·41	56·35	65·07	97·79	?
80	0·9754	31·22	37·47	58·95	75·54	90·67	142·7	?
100	0·9600	37·50	44·37	72·95	90·74	107·4	176·5	?
120	0·9444	41·03	48·78	82·58	99·28	118·0	199·8	?
140	0·9285	42·71	51·34	87·26	103·4	124·3	211·2	?
160	0·9129	43·82	52·86	89·82	106·0	127·9	217·4	?
180	0·8970	44·13	53·67	90·86	106·8	129·9	219·9	?
200	0·8813	42·62	51·06	86·26	103·0	123·6	208·6	?

TABLE II.

Acetate of d-1-Naphthyl n-hexylcarbinol.

Temperature.	D.	$[\alpha]_c$	$[\alpha]$	$[\alpha]$	$[\alpha]_j$	$[M]$	$[M]$	$[M]$	$[M]_j$	Dispersion ratios. Hg_{green}	Hg_{violet}
20°	1·0262	+23·85°	+25·05°	+28·68°	+53·10°	+67·74°	+71·15°	+81·45°	+151·0°	1·148	1·854
40	1·0110	28·15	29·56	34·07	63·18	80·05	83·95	96·67	179·4	1·153	1·854
60	0·9947	32·12	33·50	38·73	71·58	91·22	95·13	110·0	203·2	1·153	1·848
80	0·9785	35·10	36·89	42·48	79·18	99·68	104·7	120·6	224·9	1·153	1·866
100	0·9624	37·75	39·51	45·50	84·78	107·2	112·2	129·2	240·7	1·154	1·863
120	0·9460	39·64	41·78	48·09	89·41	112·6	118·7	136·6	253·9	1·154	1·859
140	0·9300	41·20	43·44	50·03	93·07	117·0	123·4	142·1	264·3	1·156	1·860
160	0·9139	42·35	44·42	51·39	95·45	120·2	126·2	145·9	271·1	1·157	1·858
180	0·8979	43·10	44·82	51·84	97·12	122·4	127·3	147·2	275·2	1·155	1·866
200	0·8815	43·34	44·84	51·40	97·90	123·1	127·4	145·6	278·1	1·153	1·903

Propionate.

Temperature.	D.	$[\alpha]_c$	$[\alpha]$	$[\alpha]$	$[\alpha]_j$	$[M]$	$[M]$	$[M]$	$[M]_j$	Hg_{green}	Hg_{violet}
20°	1·0147	28·50°	30·18°	34·69°	64·36°	85·17°	80·93°	103·4°	191·6°	1·149	1·856
40	1·0002	33·93	34·43	39·94	74·03	95·11	102·6	119·1	229·6	1·160	1·854
60	0·9850	36·65	38·13	44·39	83·91	109·2	113·8	132·3	247·4	1·162	1·869
80	0·9692	39·62	41·28	47·92	89·76	115·0	123·0	142·8	267·5	1·161	1·474
100	0·9521	42·05	43·96	50·76	95·54	125·4	131·0	151·2	254·7	1·154	1·852
120	0·9339	43·82	45·73	52·91	99·49	130·6	136·2	157·7	296·2	1·157	1·874
140	0·9150	45·17	47·20	54·70	102·7	134·6	140·6	163·0	305·9	1·159	1·878
160	0·8961	46·24	48·35	56·19	105·1	137·8	144·1	167·4	313·1	1·162	1·899
180	0·8778	47·08	49·12	57·03	107·9	140·3	146·4	169·9	318·8	1·161	1·876
200	0·8595	47·75	49·71	57·51	105·1	142·3	148·1	171·4	322·2	1·157	1·876

TABLE II (*continued*).

n-Butyrate.

Tempera-ture.	D_t	$[\alpha]_t$	$[\alpha]_t$	$[\alpha]_t$	$[\alpha]_t$	$[M]_t$	$[M]_t$	$[M]_t$	$[M]_t$	Dispersion ratios	
										Hg_{green}	Hg_{violet}
20°	1·0059	+27·32	28·16	+32·54	+60·22	+84·29°	87·88°	+101·5°	+187·9°	1·155	1·850
40	0·9909	30·71	32·15	37·16	69·34	95·83	100·3	116·0	216·4	1·156	1·866
60	0·9744	33·71	35·44	41·00	76·08	105·2	110·6	127·9	238·2	1·157	1·871
80	0·9587	36·02	37·86	44·11	81·93	112·4	118·1	137·6	255·7	1·165	1·858
100	0·9431	37·87	39·77	46·15	86·24	118·1	124·1	144·0	269·1	1·161	1·868
120	0·9273	39·13	41·22	47·69	89·02	122·1	128·6	148·8	277·7	1·157	1·871
140	0·9116	40·17	42·27	48·84	91·49	125·3	131·9	152·7	285·5	1·158	1·869
160	0·8957	41·04	43·11	49·82	93·42	128·0	134·5	155·4	291·5	1·155	1·875
180	0·8800	41·66	43·75	50·46	94·58	130·0	136·6	157·4	295·1	1·153	1·875
200	0·8643	42·01	44·10	50·71	94·99	131·6	137·6	158·2	296·4	1·150	1·874

n-Valerate.

Tempera-ture.	D_t	$[\alpha]_t$	$[\alpha]_t$	$[\alpha]_t$	$[\alpha]_t$	$[M]_t$	$[M]_t$	$[M]_t$	$[M]_t$	Dispersion ratios	
										Hg_{green}	Hg_{violet}
20°	0·9974	+22·23	+23·30	+26·73	+49·45	+72·47°	+75·96°	+87·14°	+161·2°	1·148	1·850
40	0·9816	25·42	26·65	30·71	57·68	83·85	80·86	100·1	180·0	1·153	1·878
60	0·9600	28·19	29·53	34·09	64·30	91·89	96·27	111·1	209·6	1·154	1·887
80	0·9500	30·47	31·84	36·74	69·00	99·31	103·8	119·8	224·9	1·153	1·878
100	0·9348	32·18	33·67	38·89	72·40	104·1	109·7	126·8	237·0	1·154	1·869
120	0·9191	33·47	35·10	40·52	75·88	109·1	114·4	132·1	247·4	1·154	1·873
140	0·9035	33·45	36·08	41·73	78·11	112·3	117·6	136·0	254·6	1·156	1·872
160	0·8874	35·11	36·73	42·45	79·50	114·2	118·6	138·6	259·2	1·155	1·876
180	0·8715	35·51	36·73	42·94	80·02	116·5	121·5	140·9	262·5	1·155	1·876
200	0·8569	36·09	37·33	43·04	81·07	116·5	121·7	140·0	264·2	1·153	1·884

TABLE II (continued).

n-Hexoate.

Temperature	D_4^t	$[\alpha]_L$	$[\alpha]_r$	$[\alpha]_r$	$[M]_L$	$[M]_r$	$[M]_r$	Dispersion Hg:Li
20°	0·9894	+21·12°	+22·36°		+71·81°	+76·02°		
40	0·9853	23·79	25·10		80·87	85·35		
60	0·9595	26·35	27·76		89·60	94·39		
80	0·9433	27·94	29·53		94·99	100·4		
100	0·9272	29·34	31·06		99·74	105·6		
120	0·9112	30·37	32·16		103·2	109·3		
140	0·8955	31·27	33·05	+37·74°	106·4	112·4	+128·3°	1·142
160	0·8800	32·02	33·76	38·59	108·8	114·8	131·2	1·143
180	0·8643	32·62	34·46	39·39	110·9	117·1	133·9	1·144

n-Heptoate.

Temperature	D_4^t	$[\alpha]_L$	$[\alpha]_r$	$[\alpha]_r$	$[M]_L$	$[M]_r$	$[M]_r$	Dispersion Hg:Li
20°	0·9830	+19·63°	+20·59°	+23·68°	+69·50	+72·88°	+83·83°	1·150
40	0·9074	21·97	23·31	26·46	77·75	82·52	93·67	1·135
60	0·9518	24·11	25·31	28·77	83·35	89·62	101·9	1·137
80	0·9360	25·74	26·85	30·56	91·14	95·04	108·1	1·139
100	0·9200	26·83	28·82	31·96	94·99	99·22	113·1	1·140
120	0·9042	27·50	28·59	33·93	97·34	102·1	116·9	1·146
140	0·8886	28·02	29·39	33·76	99·19	104·0	119·5	1·149
160	0·8725	28·54	29·96	34·39	101·0	104·0	121·7	1·148
180	0·8570	29·05	30·51	35·50	102·8	104·0	123·9	1·148

TABLE II (continued).

n-Octoate.

Temperature.	l	$[\alpha]$	$[\alpha]$	$[\alpha]$	$[\alpha]$	$[M]$	$[M]$	$[M]$	$[M]$	Hg_{green}	Hg_{blue}
20°	0·9797	+21·13°	+22·11°	+25·40°	+47·56°	+77·75°	+81·36°	+93·67°	+175·0°	1·153	1·868
40	0·9650	23·44	24·67	28·39	53·27	86·25	90·76	104·4	196·0	1·151	1·877
60	0·9505	25·23	26·57	30·61	57·44	92·85	97·77	112·7	211·3	1·152	1·877
80	0·9357	26·44	27·93	32·15	60·49	97·29	102·8	118·2	222·6	1·151	1·882
100	0·9210	27·36	28·85	33·19	62·38	100·7	106·2	122·1	229·6	1·150	1·879
120	0·9060	28·05	29·47	33·91	63·57	103·2	108·4	124·8	234·0	1·151	1·875
140	0·8913	28·49	29·88	34·44	64·63	104·8	110·0	126·8	237·8	1·153	1·876
160	0·8766	28·75	30·14	34·81	65·69	105·8	110·9	128·1	241·7	1·155	1·887
180	0·8617	28·89	30·34	35·03	66·70	106·3	111·6	128·9	245·4	1·154	1·904

n-Nonoate.

Temperature.	l	$[\alpha]$	$[\alpha]$	$[\alpha]$	$[\alpha]$	$[M]$	$[M]$	$[M]$	$[M]$	Hg_{green}	Hg_{blue}
20°	0·9726	+19·06°	+19·68°	+22·88°	—	+72·85°	+75·19°	+87·40°	—	1·162	—
40	0·9576	21·25	21·82	25·22	—	81·19	83·37	96·34	—	1·155	—
60	0·9425	22·80	23·45	27·16	—	87·10	89·58	103·8	—	1·158	—
80	0·9276	23·82	24·61	28·52	—	91·01	94·01	109·0	—	1·159	—
100	0·9126	24·57	25·46	29·58	—	93·85	97·27	113·0	—	1·161	—
120	0·8977	25·15	26·22	30·42	—	96·07	100·2	116·2	—	1·160	—
140	0·8830	25·60	26·75	30·99	—	96·77	102·3	118·4	—	1·158	—
160	0·8672	25·73	26·95	31·34	—	96·77	103·3	118·4	—	1·159	—
180	0·8525	26·05	26·13	31·48	—	99·45	103·7	118·2	—	1·160	—

TABLE II (continued).

n-Decoate.

Temperature.	D'₄.	[a]'ᵢ.	[a]'ⱼ.	[a]ⱼ.	[M]ⱼ.	[M]ⱼ.	[M]ⱼ.	Dispersion H₉/₀ₗ.
20°	0·9603	+17·13°	+18·09°	+20·80°	+67·82°	+71·66°	+82·37°	1·149
40	0·9540	18·89	19·82	22·88	74·81	78·47	90·59	1·153
60	0·9389	20·45	21·25	24·55	80·98	84·16	97·31	1·155
80	0·9237	21·65	22·45	25·92	85·74	88·88	102·7	1·154
100	0·9086	22·56	23·42	27·02	89·35	92·72	107·0	1·154
120	0·8937	23·18	24·08	27·86	91·81	95·39	110·4	1·157
140	0·8788	23·69	24·58	28·44	93·82	97·34	112·7	1·157
160	0·8635	24·08	25·04	28·95	95·39	99·18	114·7	1·157

n-Undecoate.

Temperature.	D'₄.	[a]'ᵢ.	[a]'ⱼ.	[a]ⱼ.	[M]ⱼ.	[M]ⱼ.	[M]ⱼ.	Dispersion H₉/₀ₗ.
20°	0·9614	+16·44°	+17·08°	+19·76°	+67·39°	+70·01°	+81·04°	1·157
40	0·9468	18·17	18·79	21·97	74·47	77·07	90·07	1·160
60	0·9325	19·63	20·24	23·28	80·48	82·09	95·43	1·164
80	0·9179	20·63	21·29	24·22	84·65	87·32	99·31	1·137
100	0·9031	21·35	22·04	25·02	87·54	90·36	102·6	1·136
120	0·8885	21·78	22·48	25·55	89·32	92·17	104·7	1·137

TABLE III.

Acetate of 1-1-Naphthylmethylcarbinol.

Temperature	D	$[\alpha]$	$[\alpha]$	$[\alpha]$	$[M]$	$[M]$	$[M]$	Dispersion. Mg violet
20°	1·1044	−32·28°	−38·90°	−73·79°	−69·07°	−83·24°	−157·9°	1·898
40	1·0898	39·51	47·47	88·04	84·55	101·6	188·4	1·858
60	1·0733	44·58	54·04	101·51	95·43	105·6	217·2	1·878
80	1·0552	49·18	59·39	113·02	105·2	127·1	241·9	1·903
100	1·0368	52·85	64·21	121·57	113·1	137·4	250·1	1·892
120	1·0185	55·22	67·07	126·02	116·1	143·5	269·7	1·879
140	1·0002	56·78	68·68	129·82	121·5	147·0	277·8	1·891
160	0·9820	68·11	70·33	132·02	124·4	150·5	283·8	1·886
180	0·9635	59·29	71·83	135·39	126·9	153·7	289·7	1·885

EXPERIMENTAL.

dl-1-*Naphthyl-n-hexylcarbinol*,
$C_{10}H_7 \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$.

The reaction between magnesium 1-naphthyl bromide and *n*-heptaldehyde proceeds smoothly only under certain conditions. The naphthyl bromide should be free from the dibromide commonly present in the commercial product, and the aldehyde should be freshly distilled. The aldehyde, dissolved in ten times its volume of ether, should be added very slowly to an excess of a dilute ethereal solution of the bromide, which is at the time reacting in slightly less than the calculated amount of magnesium, the temperature of the whole being kept at that of a mixture of ice and salt. The products of the reaction should be poured on to a mixture of ice and dilute sulphuric acid as soon as the addition of the aldehyde solution is complete, and then immediately extracted with ether. Much naphthalene being formed in the reaction it is desirable to remove it along with the ether and unchanged aldehyde by distillation in a current of steam. The residue is then dissolved in ether, carefully dried, and fractionally distilled at a pressure of 3 mm. All the carbinol is in the portion rising above 160°, whilst the lower fractions contain the corresponding unsaturated hydrocarbon and the unchanged naphthyl oxide. In one series of operations, working with 620 grams of bromide and 228 grams of *n*-heptaldehyde, the yield of carbinol was 370 grams.

dl-*Naphthyl-n-hexylcarbinol* boils at 184°/4 mm., and on keeping sets to a crystalline mass, which crystallises from light petroleum in feathery needles melting at 41--42°. When guarded from the accidental access of crystal nuclei, it will remain for some time in a supercooled condition, but solidifies rapidly when seeded.

The *hydrogen phthalate*, prepared by the method described in Part IV. (*loc. cit.*, p. 1126), is only sparingly soluble in light petroleum, and is best crystallised from a mixture of this and acetone, from which it separates in slender needles melting at 103--104°:

0.2245 neutralised 0·0226 NaOH. M.W. = 397. Calc. M.W. 390.

Resolution of Hydrogen Phthalate.

The fractional crystallisation from acetone of the brucine salts of the (*d + l*) phthalic ester yields readily the salt of the *d* ester, the process being carried out in the manner previously described in detail (see *inter alia*, T., 1912, **101**, 634). The ester (514 grams)

was dissolved in warm acetone (1½ litres), digested with bone (614 grams), and set aside to crystallise. The first crop weighed 300 grams, and was then recrystallised six times. The second crop weighed 160 grams, and was the pure *l*B*d*A salt, which melted and decomposes at 124—125°. Two successive series of operations with the mother liquors comprising respectively eight and ten crystallisations yielded further lots of the salt amounting to 34 and 15 grams respectively.   Samples of the salt from the fifth and seventh crops of the first series of crystallisations and from the final crops of the second and third series yielded hydrogen phthalates which had respectively [α]$_D$ −23·01°, −22·46°, and −22·62° respectively in (approximately) 5 per cent. ethyl alcohol solution.

d-1-*Naphthyl*-n-*hexylcarbinol* boils at 178°/3 mm., solidifies in stellate nodules, and melts at 41·5°.

The corresponding d-*hydrogen phthalate* solidifies in crystalline nodules, melts at 91°, and is soluble in all the common organic media.   The crystalline *sodium* salt, which was obtained by neutralisation of a solution of the ester in methyl alcohol with sodium methoxide and subsequent removal of the solvent in a desiccator, is decomposed by water.

Normal Esters of the Carbinol.—Of the esters prepared (see table IV) the acetate, propionate, and n-butyrate were obtained by the interaction of the carbinol and the respective anhydrides, and the others were prepared by the action of the respective acid chlorides on solutions of the carbinol in pyridine.   They are all viscous liquids at the ordinary temperature, and have no odour, but the higher members of the series often develop a faint greenish bloom, which is difficult to remove by redistillation, thus rendering uncertain any polarimetric readings in the green, and particularly in the violet portions of the spectrum.

TABLE IV.

Esters of d-1-*Naphthyl*-n-*hexylcarbinol.*

	B. p.	D$_4^{20}$.	n_D^{20}.	$(n-1)/d.M.$	[α]$_D$.	M$_A^2$
Acetate	167°/2·5 mm.	1·0262	1·5471	151·3	+23·85	·67·3
Propionate ...	169°/2 ,,	1·0147	1·5403	158·7	26·59	63·8
n-Butyrate ...	184°/3 ,,	1·0050	1·5365	166·6	27·02	44·3
n-Valerate ...	187°/2·5 ,,	0·9974	1·5332	174·3	22·23	73·6
n-Hexoate ...	198°/2·5 ,,	0·9894	1·5289	181·8	21·42	73·8
n-Heptoate ...	207°/3 ,,	0·9830	1·5271	189·8	19·63	54·4
n-Octoate	214°/3 ,,	0·9797	1·5249	197·1	21·13	73·3
n-Nonoate......	222°/4 ,,	0·9726	1·5225	205·2	19·06	73·6
n-Decoate ...	224°/2·5 ,,	0·9693	1·5208	213·0	17·13	63·4
n-Undecoate...	232°/2·5 ,,	0·9614	1·5188	221·0	16·44	67·3

d-1 Naphthylen hexylcarbinol

Solvent	Length of tube, cm	Weight of solute in grams.	$a_{...}$	$a_{...}$	$a_{...}$	$[a]_{...}$	$[a]_{...}$	$[a]_{...}$	$[M]_{...}$	$[M]_{...}$	$[M]_{...}$	$[M]_{...}$	Dispersion.
Benzene	22	1·0589	+8·70°	+10·48°	+18·25°	+74·67°	+89·97°	+156·7°	+180·7°	+217·7°	+379·1°		1·742
Acetone	10	0·6687	2·39	2·80	5·20	71·48	85·54	155·5	172·9	207·0	376·2		1·818
Ethyl alcohol	22	1·0666	7·69	9·39	16·52	85·37	80·02	140·8	158·2	193·6	340·6		1·759
Chloroform	22	1·0952	7·80	9·40	16·41	04·76	78·03	136·2	166·7	188·8	329·7		1·748
Carbon disulphide	22	0·9686	6·41	7·73	13·30	60·15	72·52	124·8	145·5	175·6	302·0		1·721
Ethylene dibromide	10	0·9210	2·51	2·95	5·30	54·46	64·00	115·0	131·8	154·9	278·2		1·797
Pyridine	20	1·0340	4·38	5·23	9·02	42·36	50·58	87·24	102·5	122·4	211·2		1·725

Hydrogen Phthalate.

Solvent	Length of tube, cm	Weight of solute in grams.	$a_{...}$	$a_{...}$	$a_{...}$	$[a]_{...}$	$[a]_{...}$	$[a]_{...}$	$[M]_{...}$	$[M]_{...}$	$[M]_{...}$	$[M]_{...}$	Dispersion.
Carbon disulphide	22	1·0106	8·37	10·09	18·90	75·26	90·72	170·0	293·6	353·8	663·0		1·474
Acetic acid	22	0·9900	2·75	3·23	5·22	25·25	29·66	47·94	98·49	115·7	186·9		1·616
Chloroform	22	1·1846	2·28	2·71	4·22	17·50	20·80	32·38	68·23	41·12	126·3		1·655
Benzene	22	1·0917	0·60	0·57	0·12	5·00	4·74	1·00	19·48	14·51	3·30		2·105
Pyridine	22	1·0454	-0·15	-0·36	-1·28	-1·30	-3·13	-11·14	-5·09	-12·22	-43·43		3·555
Ethyl alcohol	22	1·0326	-2·55	-3·25	-6·93	-22·46	-28·63	-61·02	-87·58	111·6	-238·0		2·132

Sodium Salt of the Hydrogen Phthalate.

| Ethyl alcohol | 22 | 1·0595 | +3·50 | +4·14 | -7·37 | -29·35 | -35·52 | +63·24 | +120·9 | -146·3 | -280·5 | | 1·790 |

Brucine Salt of the Hydrogen Phthalate.

| Ethyl alcohol | 22 | 1·0826 | -1·45 | -2·07 | -5·62 | -12·81 | -17·39 | -47·21 | -95·59 | 136·3 | -276·1 | | 2·714 |

All solutions for the determinations of rotatory power recorded in this paper were prepared by making up about 1 gram of the substance to 20 c.c. with the solvent at the temperature of the laboratory, at which temperature all observations were made.

TABLE VI.

Determination of the Rotatory Powers of the Esters in (approx.) 5 per cent. Solution in Ethyl Alcohol.

Ester	Length of tube, cm.	Weight of solute in grams.	a_1	a_2	a_3	a_4	$[a]_1$	$[a]_2$	$[a]_3$	$[a]_4$	$[M]_1$	$[M]_2$	$[M]_3$	$[M]_4$	Dispersion $\frac{Hg\,violet}{Hg\,green}$
Acetate	20	1·1363	+3·84°	+4·02°	+4·64°	+8·62°	33·80°	+35·38°	40·84°	+75·88°	+95·98°	+100·5°	+116·0°	+215·5°	1·858
Propionate	20	0·9503	3·45	3·60	4·17	7·65	36·31	37·88	43·88	80·52	108·1	112·9	130·8	240·0	1·835
Butyrate	22	1·1019	3·90	4·08	4·70	8·70	32·18	33·66	38·77	71·76	100·4	105·1	121·0	224·0	1·851
Valerate	20	1·1392	3·10	3·34	3·76	7·04	27·21	29·32	33·01	61·80	88·72	95·57	107·6	201·5	1·873
Hexoate	20	0·9768	2·50	2·67	3·05	5·85	26·52	27·33	31·23	59·89	90·16	92·94	106·2	203·6	1·918
Heptoate	20	0·9887	2·30	2·44	2·76	5·10	23·26	24·68	27·91	51·58	82·33	87·36	98·81	182·6	1·848
Octoate	20	0·9020	2·28	2·37	2·72	5·12	25·27	26·27	30·16	58·76	93·01	96·68	111·0	203·8	1·883
Nonoate	20	1·1589	2·55	2·65	3·05	5·74	22·01	22·87	26·32	49·53	84·07	87·36	100·6	180·2	1·883
Decoate	22	1·0601	2·15	2·27	2·53	—	19·54	20·64	23·00	—	77·30	81·72	91·07	—	—
Undecoate	20	1·1233	2·02	2·12	2·41	4·80	17·90	18·88	21·60	42·74	73·76	77·30	87·08	175·2	1·902

TABLE VII.

Determination of the Rotatory Powers of the Esters in (approx.) 5 per cent. Solution in Carbon Disulphide.

Ester	Length of tube, cm.	Weight of solute in grams.	a_D	a_r	a_c	a_r	$[a]_D$	$[a]_r$	$[a]_D$	$[a]_r$	$[M]_D$	$[M]_r$	$[M]_D$	$[M]_r$	Dispersion $Hg \ldots$
Acetate	22	1·1254	13·80	14·51	16·95	33·10	111·5	117·3	137·0	208·2	316·7	333·1	389·0	761·7	1·914
Propionate	20	1·0157	12·48	13·12	15·31	29·83	122·8	129·1	150·7	293·6	366·0	384·9	449·0	874·8	1·948
Butyrate	20	1·0665	12·05	12·74	14·84	29·12	113·1	119·3	139·3	273·2	352·8	373·0	434·5	852·5	1·962
Valerate	20	0·9541	9·70	10·32	12·07	23·58	102·7	108·4	126·6	247·3	333·6	352·7	412·5	866·0	1·954
Hexoate	10	0·9483	4·70	4·87	5·68	11·40	99·10	102·7	119·8	240·4	327·0	349·1	467·1	817·4	2·065
Heptoate	10	1·2190	5·47	5·59	6·72	13·25	89·74	94·99	110·3	217·4	317·7	338·2	390·3	769·5	1·952
Octoate	10	1·0342	4·46	4·71	5·49	10·55	86·64	91·67	106·2	205·9	318·8	335·2	389·6	764·9	1·958
Nonoate	10	1·0299	4·29	4·52	5·34	10·40	84·06	88·54	104·6	203·8	321·0	348·2	399·6	775·2	1·945
Decoate.............	20	1·0573	8·43	8·87	10·36	21·50	75·36	82·35	99·20	190·6	310·3	326·1	387·0	790·5	2·075
Undecoate	22	1·0180	7·31	7·74	10·19	20·50	74·22	78·05	96·99	182·1	304·3	329·0	373·1	750·8	2·012

Determinations of Density (D'$_4$) and Rotatory Power (α^x ···) the Carbinol and Esters in the Homogeneous State.

The procedure in the determinations of rotatory ···· density was the same as described in Part VIII. (this v··· ···

d-1-Naphthyl-n-hexylcarbinol.

Temp.	31	63°	91°	146°
D$_4$	1·0147	0·9890	0·9668	0·9234

Temp. 15	24	26·5	28	36°	38°	42·5°	44	49
α$_u$ ... −6·04	÷3·26	3·88	4·56	10·12°	11·40°	13·60°	14·94	17·5
53	58	64°	76	98	104°	119°	145	169
+20·00	22·00	25·14	29·10	35·72	36·52	38·80°	39·60	40·46

Temp. 15	24	25	26·5	28	32·5°	39°	43
α$_{gr}$ ...... −8·12	÷2·30	2·48	3·54°	4·78°	8·20°	12·90°	16·52
49°	55	58	69	103·5	125°	145°	168	199
20·32	23·70	25·34	31·86	43·34	46·80°	47·90°	48·30	45·46

Temp. 15°	24	25	26·5	28	32°	39°	43	50
α$_{vi}$ ... −24·82	−6·00	5·06	−3·34	−0·76	5·10°	14·24	21·48	25·5
56°	58	69	73	104°	125°	143°	169	195
36·42°	37·48°	49·42	50·90	72·20°	79·20°	81·04°	81·90	76·16

Acetate of d-1-Naphthyl-n-hexylcarbinol.

Temp.	19·5	54	90°	132°
D'$_4$	1·0266	1·0001	0·9699	0·9371

Temp.	21°	47	83°	104°	123°	154	18·
α$_b$	÷24·56	29·90	34·58°	36·08	37·58	38·64	38·
Temp.	21°	49	83°	104°	123°	158	18·
α$_{yellow}$	÷25·96	31·54	36·50	38·26°	39·68	40·58	58·
Temp.	21°	49°	83	104°	123°	153	18·
α$_{gr}$	29·72	36·50	42·00	44·10	45·66	46·90	48·
Temp.	21°	49·5	83	104°	123°	158	18·
α$_{vi}$	+54·88	67·42	78·30	82·18°	85·00	87·20	87·

Propionate.

Temp.	20·5°	56°	94°	134°
D'$_4$	1·0144	0·9885	0·9574	0·9208

Temp.	24°	54°	68°	97°	123°	153	18·
α$_b$	29·96°	35·32°	37·08°	39·88°	41·00°	41·40	43·
Temp.	24°	52°	75°	96°	123°	152	18·
α$_{yellow}$	+31·42°	36·56°	39·30°	41·80°	42·70°	43·30	43·
Temp.	24°	52°	76°	96°	123°	152	18·
α$_{gr}$	+36·26	42·46°	45·86°	48·04°	49·46°	50·24	43·
Temp.	24°	51°	76°	96°	123°	152	18·
α$_{vi}$	+67·80	79·00°	86·10°	90·30°	92·96°	94·16	93·

n-Butyrate.

18°	61°	97°	134·5				
1·0066	0·9739	0·9459	0·9155				

20°	30°	60°	85°	105°	121°	163°	195°
-27·12°	28·94°	32·78°	34·86°	35·92	36·28	36·76	36·42

20°	57°	85°	105°	121°	163°	195°
-28·30°	34·26°	36·60°	37·78°	38·48°	38·56	38·18
-32·70°	39·54°	42·50°	43·60°	44·34	44·60	44·62

20°	56°	84°	105°	121	163	195
-60·50°	73·70°	79·20°	81·90°	82·78	83·66	82·46

n-Valerate.

20·5°	56·5°	93°	132°			
0·9956	0·9694	0·9410	0·9088			

23°	45°	65°	87°	119°	138	182
-22·58°	25·68°	27·68	29·38°	30·72	31·10	30·90

23°	47°	87	120°	138	182
-23·68°	27·01°	30·74	32·26	32·56	32·32

23°	47°	87	121°	138°	182
-27·28°	31·22°	35·48	37·26°	37·66	37·38

23°	47°	87°	122°	138	182
-50·70°	58·80°	66·42°	69·84	70·58	70·08

n-Hexoate.

19°	57°	97°	146°				
0·9897	0·9636	0·9285	0·8911				

20°	48°	60°	72°	107°	130	152	170°
-20·90°	24·36°	25·30°	25·90°	27·40	27·80	28·14	28·16

20°	49°	58°	76°	109°	129	153	170
-22·12°	25·80°	26·46°	27·68°	29·16	29·38	29·70	29·74

n-Heptoate.

....	18°	53·5°	97°	141°	
....	0·9825	0·9584	0·9220	0·8874	

....	20°	56°	82°	114°	148°
....	+19·30°	22·66°	24·18°	24·84	24·92

....	20°	53°	87°	116°	148°
....	+20·24°	23·66°	25·40°	26·04	26·14

....	20°	52°	86°	117°	148°
....	+23·28	26·76	28·88	29·82°	30·00

n-Octoate.

....	18°	55°	92°	144·5°
....	0·9806	0·9549	0·9263	0·8880

n-*Octoate* (continued).

Temp.	20°	44°	58°	69°	88°	120°	145	ᵒᵈ
a_D	20·70°	22·94°	23·84°	24·36°	24·80°	25·50°	25·54	5···

Temp.	20°	45°	68°	91°	118°	145		
a_{yellow}	21·66°	24·24°	25·80°	26·00°	26·76°	26·52		
a_{gr}	24·94°	27·88	29·84°	29·96°	30·74°	30·68		

Temp.	20°	45°	67°	90°	117°	143	
a_b	46·60	52·28°	55·74°	56·48°	57·60°	57·60	

n-*Nonoate*.

Temp. ...	17	59	95°	144·5°
D_4'	0·9734	0·9442	0·9157	0·8800

Temp. ...	18	35°	77°	98°	136	ᵒᵈ⁷
a_D	· 18·30°	20·20°	21·92°	22·40°	22·60	22·4

Temp. ...	18	58°	71°	101°	136	15·
a_{yellow} ...	· 18·92°	22·00°	22·60°	23·24°	23·64	·5·6

Temp. ...	18	60	74°	101°	136	15·
a_{gr}	22·00	25·60	26·26°	27·00°	27·38	2·5

n-*Decoate*.

Temp.	20·5°	58°	94°	13·
D_4'	0·9674	0·9410	0·9137	· 0·88··

Temp.	20°	56°	95°	13·
a_D	· 16·60°	19·00°	20·40°	20·7·

Temp.	20°	49°	95°	13·
a_{yellow}	· 17·54°	19·38°	21·18°	21·60
a_{gr}	20·16°	22·46°	24·44°	25·00

n-*Undecoate*.

Temp.	20·5°	58°	94°	1·3
D_4'	0·9605	0·9341	0·9075	0·87·3

Temp.	20°	61°	94°	
a_D	+15·80°	18·36°	19·22°	
a_{yellow}	+16·42°	18·94°	19·84°	
a_{gr}	+19·00°	21·74°	22·54	

Acetate of 1·1·*Naphthylmethylcarbinol*

Temp.	16°	64°	99°	138°
D_4'	1·1071	1·0699	1·0380	1·0019

Temp.	27°	36°	56°	100°	136	160
a_D	−38·66°	41·84°	46·90°	54·80°	56·70	57·00

Temp.	19°	27°	36°	61°	78	101	13·
a_{gr}	−42·70°	47·02°	50·10°	58·32°	62·26°	66·84	68·9· ··

Temp.	27°	34°	62°	76°	100°	136	1·4
a_{bl}	−87·30°	91·90°	110·30°	115·30°	126·00°	129·66	150··

every case these esters were found to have undergone no
.... during the heating in the polarimeter tube, whilst all
..... when hydrolysed yielded samples of the carbinols of
...ary power identical with that of the original preparations.

XLIX.—*Carboxylic Acids Derived from cycloButane, cycloPentane, cycloHexane, and cycloHeptane.*

By LEONARD JAMES GOLDSWORTHY and
WILLIAM HENRY PERKIN, jun.

present investigation is one of a series which has been insti-
... with the object of obtaining further evidence relating to the
...ative readiness of formation and stability of cyclic struc-
... containing varying numbers of carbon atoms. Judging by the
... produced in analogous reactions, experience is roughly in
...dance with Baeyer's "Spannungstheorie," and seems to indi-
... that, in the *cyclo*propane, *cyclo*butane, *cyclo*pentane, and
...exane series, derivatives of *cyclo*propane are produced with
...atest difficulty, and that, whilst derivatives of *cyclo*butane
...*cyclo*hexane are much more readily obtained, the tendency to
... *cyclo*pentane derivatives is so pronounced that these are
... produced in quantitative yields, and not infrequently during
...ess which might be expected to lead to the formation of
... ring complexes. The evidence on this point, however, is often
...ting, since it has frequently been observed that, although
... cyclic derivatives are obtained in very small yields, other
...tives of the same ring seem to be produced under very similar
...tions with great readiness. Thus the yield of ethyl *cyclo*
...ane 1-dicarboxylate (I) obtained when ethylene dibromide
... with the sodium derivative of ethyl malonate is very small,
...as ethyl *cyclo*propane-1 : 2-dicarboxylate (II) is readily pre-

pared in good yield when ethylene dibromide is replaced by an αβ-dibromopropionate in this interaction:

$$CH_2 \begin{matrix} C(CO_2Et)_2 \\ CH_2 \end{matrix} \qquad\qquad CH_2 \begin{matrix} CH \cdot CO_2Et \\ CH \cdot CO_2Et \end{matrix}$$
(I.)   (II.)

Other similar cases have been observed, and one of the difficulties which arises is to distinguish between the effect on the yield of the reactivity of the interacting substances on the one hand and of the readiness of formation of the closed ring on the other.

It is clear that a useful generalisation cannot be formed until a much larger number of cyclic carboxylic acids and derivatives have been prepared and investigated, and, in the present communication, we describe some new carboxylic acids from *cyclo*-butane, -pentane, -hexane, and -heptane. In the first place, we have prepared the *cis*- and *trans*-modifications of *butane*-1:2:3-*tricarboxylic acid*,

$$CH_2 \begin{matrix} CH(CO_2H) \\ CH(CO_2H) \end{matrix} CH \cdot CO_2H,$$
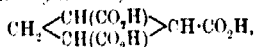
by causing ethyl αβ-dibromopropionate to react with the sodium derivative of ethyl ethanetetracarboxylate, when the reaction proceeds to the extent of about 50 per cent. in the required direction:

$$\begin{matrix} CO_2Et \cdot CHBr \\ CH_2Br \end{matrix} + \begin{matrix} NaC(CO_2Et)_2 \\ NaC(CO_2Et)_2 \end{matrix} = \begin{matrix} CO_2Et \cdot CH-C(CO_2Et)_2 \\ CH_2 \cdot C(CO_2Et)_2 \end{matrix} + Na$$

The product, after hydrolysis and elimination of carbon dioxide by heating at 190°, yields cis-cyclo*butane*-1:2:3-tricarboxylic acid (m. p. 141—143°), and this, when heated with hydrochloric acid at 180°, is converted into the *trans*-acid, which melts at 166—167°

In the *cyclo*pentane series the *cis*- and *trans*-modifications of 1:2:4-tricarboxylic acid have already been prepared from the disodium derivative of ethyl pentane-ααγγεε-hexacarboxylate by the action of iodine and subsequent hydrolysis and elimination of carbon dioxide:

$$C(CO_2Et)_2 \begin{matrix} CH_2 \cdot CNa(CO_2Et)_2 \\ CH_2 \cdot CNa(CO_2Et)_2 \end{matrix} \rightarrow C(CO_2Et)_2 \begin{matrix} CH \cdot C(CO_2Et)_2 \\ CH_2 \cdot C(CO_2Et)_2 \end{matrix}$$

$$CO_2H \cdot CH \begin{matrix} CH_2 \cdot CH \cdot CO_2H \\ CH_2 \cdot CH \cdot CO_2H \end{matrix}$$
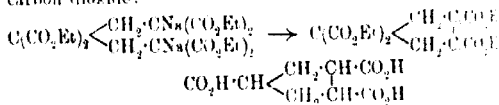
(Bottomley and Perkin, T., 1900, **77**, 296). We have succeeded in obtaining the same acids much more conveniently and in a much better yield by the action of ethyl αβ-dibromopropionate on the disodium derivative of ethyl propane-ααγγ-tetracarboxylate (ethyl methylenedimalonate):

$$\begin{matrix} CNa(CO_2Et)_2 \cdot CH_2 \cdot CNa(CO_2Et)_2 \\ CH_2Br \cdot CHBr \cdot CO_2Et \end{matrix} \rightarrow C(CO_2Et)_2 \begin{matrix} CH \cdot C(CO_2Et)_2 \\ CH_2 \cdot CH \cdot CO_2Et \end{matrix}$$
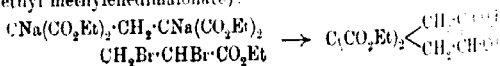
When the product of this interaction is hydrolysed, simultaneous elimination of one molecule of carbon dioxide takes place and a crystalline *cyclo*pentanetetracarboxylic acid is formed. The crude acid decomposes at 180°, and yields a syrupy mass, from which pure *cyclo*pentane-1:2:4-tricarboxylic acid is obtained by the action of hydrochloric acid at 190°. It melts at 127—130°, and is converted, by heating with acetic anhydride and subsequent distillation, into the anhydro-*cis*-acid:

$$CO_2H\cdot CH{<}^{CH_2\cdot CH\cdot CO}_{CH_2\cdot CH\cdot CO}{>}O,$$
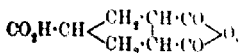
a highly characteristic derivative, which melts at 215—217°, and furnishes the *cis*-acid (m. p. 146—148°) on hydrolysis.

We next attempted the synthesis of *cyclo*hexane-1:2:4-*tricarboxylic acid* (hexahydrotrimellitic acid),

$$CO_2H\cdot CH{<}^{CH_2-----CH_2}_{CH_2\cdot CH(CO_2H)}{>}CH\cdot CO_2H,$$
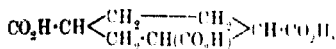
and which does not appear to have been previously described, but we ultimately succeeded in the following manner. The disodium derivative of ethyl butanetetracarboxylate was caused to react with ethyl *αβ*-dibromopropionate, when decomposition takes place in the following manner:

$$\begin{array}{l}C Na(CO_2Et)_2\cdot CH_2\cdot CH_2\cdot CNa(CO_2Et)_2\\ \quad CH_2Br\cdot CHBr\cdot CO_2Et\end{array}{\longrightarrow}$$

$$C(CO_2Et)_2{<}^{CH_2-----CH_2}_{CH_2\cdot CH(CO_2Et)}{>}C(CO_2Et)_2.$$
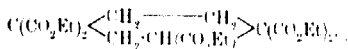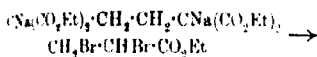
The ester thus produced yields, on hydrolysis and elimination of carbon dioxide, a mixture of stereoisomeric acids, from which, by heating with hydrochloric acid at 190°, trans-*cyclo*hexane-1:2:4-carboxylic acid was isolated, melting at 220—222°. When this acid was digested with acetic anhydride and the product distilled, most of it decomposed, but a small quantity of a distillate was obtained, which, on hydrolysis, yielded the *cis*-acid as a crystalline solid melting at 225°. It is remarkable that the *cis*- and *trans*-modifications of this acid should have almost identical melting points, and be so very similar in other properties that it was at first thought that they were identical.

However, a mixture of equal parts of the two preparations was found to soften at 198—200°, and to be almost completely melted at 205°, so that they cannot be identical, and there can be little doubt that they are the *cis*- and *trans*-modifications of *cyclo*hexane-1:2:4-tricarboxylic acid.

Finally, we have succeeded in synthesising trans-c~~y~~ ~~cyclo~~~~~~
1 : 2 : 4-*tricarboxylic acid* :

$$CO_2H \cdot CH \overset{CH_2-CH_2-CH_2}{\underset{CH_2 \cdot CH(CO_2H)}{\Big<}} CH \cdot CO_2H$$
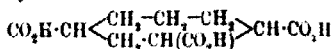
one of the few derivatives of *cyclo*heptane which have ~~been~~
obtained. For the purpose of this synthesis, the di~~sodium~~ ~~deriv~~
ative of ethyl pentane-*aaεε*-tetracarboxylate was digeste~~d with~~ ~~ethyl~~
αβ-dibromopropionate when a complicated reaction to~~ok place~~
an ester, evidently ethyl *cyclo*pentane-1 : 1 : 2 : 4 : 4-penta~~carboxylate~~
was produced in small quantity according to the equat~~ion:~~

$$CNa(CO_2Et)_2 \cdot CH_2 \cdot CH_2 \cdot CH \cdot CNa(CO_2Et)_2 \longrightarrow$$
$$CH_2Br \cdot CHBr \cdot CO_2Et$$

$$C(CO_2Et)_2 \overset{CH_2-CH_2-CH_2}{\underset{CH_2 \cdot CH \cdot CO_2Et}{\Big<}} \ldots$$
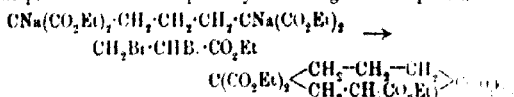
When the product of this interaction was hydrolysed, ~~the~~ ~~
acid mixture heated at 200° and then esterified, it yiel~~ded a small~~
quantity of *ethyl* cyclo*heptane*-1 : 2 : 4-*tricarboxylate* ~~(b.p.~~
212—215°/30 mm.).

On hydrolysis a syrupy mixture of stereoisomeric ~~acids~~
was obtained, from which, by heating with hydrochlor~~ic acid at~~
190°, trans-cyclo*heptane*-1 : 2 : 4-*tricarboxylic acid* was is~~olated, melt-~~
ing at 198—200°.

Apparently there is little tendency in the direction of ~~the forma-~~
tion of the *cyclo*heptane ring, since the yield of the a~~bove acid was~~
so small that we were unable to examine it at all ~~completely.~~
Further experiments, which are in progress, will show w~~hether this~~
ring and also the *cyclo*-octane and still larger rings are ~~also~~
produced with more difficulty than the simpler rings ~~containing~~
three, four, five, and six carbon atoms.

EXPERIMENTAL.

Preparation of Ethyl αβ-Dibromopropionate, $CH_2Br \cdot CHBr \cdot CO_2Et$

During the course of this and other investigations, lar~~ge quanti-~~
ties of ethyl *αβ*-dibromopropionate were required, and, as ~~the price~~
charged for this ester is prohibitive, we have made ~~a series of~~
comparative experiments on the best conditions for its ~~preparation~~
and find that the following process works well. Allyl a~~lcohol*~~
(180 grams or 210 c.c.) is mixed with an equal volume ~~of chloro-~~
form (or carbon disulphide), the solution cooled in i~~ce and~~

* Crude commercial allyl alcohol contains a large amount of water, ~~and if to be~~
used as the starting-point, it is shaken with potassium carbonate ~~as long as~~
dissolved, the aqueous layer run off and the alcohol dehydrated w~~ith a fresh~~
quantity of potassium carbonate. It is then fractionated with an ~~efficient still,~~
the portion distilling at 95—98° was collected for use in the above ~~process.~~

the bromine (496 grams or 156 c.c.) is gradually added, care
being taken that the temperature remains below 5°. The chloro-
is then removed by distillation from the water-bath under
diminished pressure, and the residual crude dibromo-propyl alcohol
need not be fractionated, but can be directly oxidised to $\alpha\beta$-dibromo-
propionic acid. The crude dibromo-alcohol (150 grams) is mixed
with ordinary concentrated nitric acid (210 grams or 1 at c.c.) and
fuming nitric acid (90 grams or 60 c.c. of 1·45) in a capacious
flask provided with a ground-in condenser and placed in water, and
the water is then very gradually heated. As soon as the initial
violent reaction has subsided, the water is raised to the boiling
point and maintained at that for seven hours; the product is then
set overnight in the ice-chest to cool, when the dibromopropionic
acid usually crystallises, but, if not, the heating is continued and
the mass seeded. The acid is collected on a Buchner funnel without
a paper, drained on porous porcelain, and a further quantity
can be obtained by concentrating the mother liquors, so that the
yield is about 75 per cent. of that theoretically possible. In
order to obtain the ethyl ester, the acid is dissolved in one and
a-half times its own weight of a 10 per cent. solution of sulphuric
acid in alcohol and heated on the water-bath for six hours. Water
then added, the heavy ester extracted with ether, the ethereal
solution washed first with dilute sodium carbonate, then with
water, dried, and the ether distilled off. The residual ethyl $\alpha\beta$-di-
bromopropionate distils almost completely at 110—150° (22 mm.,
and this was the material used in the following experiments.

cis- and *trans-cycloButane* 1 : 2 : 3 *tricarboxylic Acids,*

$$CH_2 <^{CH(CO_2H)}_{CH(CO_2H)} > CH \cdot CO_2H.$$
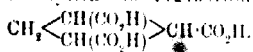
In order to obtain these acids, the first step was the synthesis of
ethyl *cyclo*butane-1 : 1 : 2 : 2 : 3-pentacarboxylate (p. 2666), and this
was accomplished in the following way: Ethyl ethanetetracarb-
oxylate (31 grams) was mixed with a little alcohol,[*] and then with
a solution of sodium (4·6 grams) in alcohol (100 c.c.), and, after
passing for a few minutes until the whole of the ester had passed
into solution, ethyl $\alpha\beta$-dibromopropionate (27 grams) was gradually
added. In a short time the mixture became warm, copious pre-
cipitation of sodium bromide took place, and the process was com-
pleted by heating in a soda-water bottle in boiling water for four
hours. The product was mixed with water, extracted with ether,
the ethereal solution washed well, dried, and the ether distilled off.

The crude ester which appears to distil at about 230° ....
not be purified before conversion into *cyclo*butanetricarb........
but is at once hydrolysed by boiling with 50 per cent. ....
25 per cent. methyl-alcoholic potassium hydroxide for four ....

Water is then added, the product evaporated until ....
from methyl alcohol, the solution is then acidified with con....
concentrated hydrochloric acid, evaporated to dryness ....
residue extracted with ether in a Soxhlet apparatus. After ....
ling off the ether, crude *cyclo*butanepentacarboxylic acid rem....
a slightly brown, viscid syrup, and this is heated in an oil ....
190° for one hour, when the evolution of carbon dioxide ....
ceased. The acid which remains does not readily crystall....
therefore purified by conversion into the ester which is obt....
boiling the acid with ten times its weight of 10 per cent. ....
sulphuric acid in a reflux apparatus for seven hours. The ....
is diluted with water, extracted with ether, the ethereal ....
washed well with sodium carbonate, dried, and evaporated ....
residue fractionated under 40 mm. pressure. A small quantity ..
oil passes over below 190°, and probably contains ethyl ....
then almost the whole of the remainder distils at 190—205°/40 ..
refractionation, pure *ethyl* cis-*cyclobutane*-1:2:3-*tricarb*....
obtained as a colourless oil boiling at 195—197°/40 mm. ..

0·2246 gave 0·4714 CO_2 and 0·1540 H_2O. C = 57·2; H = 7·6

$C_{15}H_{20}O_6$ requires C = 57·3; H = 7·3 per cent.

In the preparation of the tricarboxylic acid, the ester de....
at 190—205°/40 mm. was hydrolysed by boiling with some ....
25 per cent. methyl-alcoholic potassium hydroxide for four ..
Water was then added, the solution evaporated until free ..
from methyl alcohol, mixed with excess of hydrochloric ac ..
porated, and the dry residue extracted with ether in a ..
apparatus. The ethereal solution deposited, after boiling ....
ether, a solid acid, which was left in contact with porous ..
and then recrystallised from concentrated hydrochloric acid.

0·1410 gave 0·2332 CO_2 and 0·0592 H_2O. C = 45·1; H = 4·6

$C_7H_8O_6$ requires C = 44·7; H = 4·3 per cent.

On titration, 0·1226 required 0·0772 NaOH for neutralis....
whereas this amount of a tribasic acid, $C_7H_8O_6$, should ....
0·0782 NaOH.

cis-*cycloButane*-1:2:3-*tricarboxylic acid* melts at 141—143°
is readily soluble in water or alcohol, but rather sparingly ..
cold concentrated hydrochloric acid.

In order to obtain the *trans*-modification, the cis-acid ..
was heated with concentrated hydrochloric acid (15 c.c.) in a ..
tube at 180° for two hours. After diluting with water and ..

a trace of carbonaceous matter, the solution was concentrated, on standing over solid potassium hydroxide, a hard, glassy, gelatine mass, consisting of flat, glistening plates, gradually separated:

0·31 gave 0·1699 CO_2 and 0·0111 H_2O. C = 44·9; H = 4·4.

$C_7H_8O_6$ requires C = 44·7; H = 4·2 per cent.

By titration, 0·3500 neutralised 0·2236 NaOH, whereas this amount of a tribasic acid, $C_7H_8O_6$, should neutralise 0·2234 NaOH. trans-cyclo*Butane*-1:2:3-*tricarboxylic acid* melts at 168—170°, is readily soluble in water, but sparingly so in concentrated hydrochloric acid. The solution of the acid in excess of ammonia gives, when boiled with barium chloride, a very sparingly soluble barium salt, and the *cis*-acid behaves in a similar manner. Both acids are oxidised with difficulty, even when their alkaline solutions are boiled with permanganate.

Trianilide of the trans-*Acid*. In order to prepare this deriv-ative, the pure *trans*-acid was heated with thionyl chloride in a sealed tube at 100° for an hour; the product was then evaporated, the residual syrup dissolved in benzene. Aniline was added in excess, and, as soon as the vigorous action had subsided, the benzene was evaporated, the mass treated with dilute hydrochloric acid and the precipitate collected and drained on porous porcelain. The *trianilide* of trans-cyclobutane-1:2:3-*tricarboxylic acid* melts at 225°, and separates from alcohol, in which it is sparingly soluble, as a voluminous, almost gelatinous, mass of needles. For analysis it was recrystallised by dissolving in acetone and adding benzene; the acetone was then distilled off, and the solution set aside, when the substance separated as a crystalline crust of needles:

0·249 gave 21·5 c.c. N_2 at 17° and 763 mm. N = 10·2.

$C_{25}H_{23}O_3N_3$ requires N = 10·2 per cent.

In order to make sure that transformation of the *trans*-acid into a *cis*-modification had not taken place during the heating with thionyl chloride, some of the syrupy product of this action was decomposed by boiling with water and the acid recrystallised, when it melted at 168—170°.

The cis- and trans-cyclo*Pentane*-1:2:4-*tricarboxylic Acids*,

$$CO_2H\cdot CH\!\!<\!\!\begin{array}{l}CH_2\cdot CH\cdot CO_2H\\CH_2\cdot CH\cdot CO_2H\end{array}$$
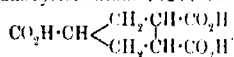
The ethyl *cyclo*pentane-1:1:2:4:4-pentacarboxylate employed in the synthesis of these acids was obtained under the following conditions.

Ethyl methylenedimalonate, $(CO_2Et)_2CH\cdot CH_2\cdot CH(CO_2Et)_2$ (33·2

grams), dissolved in alcohol (50 c.c.) was added to a co[...]
sodium (4·6 grams) in alcohol (100 c.c.), and, after a [...]
the disodium derivative was mixed with ethyl αβ-dibr[...]
(26 grams), when gradual rise of temperature, follow[...]
ous action, set in, and sodium bromide separated. [...]
was completed by heating for three hours in a soda w[...]
the product was diluted with water, extracted with eth[...]
washing well, drying, and evaporating off the ether, th[...]
was distilled, when almost the whole quantity pass[...]
226—240°/15 mm., and, on redistillation, the boiling [...]
ethyl *cyclo*pentanepentacarboxylate was observed [...]
234—236°/15 mm. The ester was hydrolysed in the [...]
by boiling with excess of 25 per cent. methyl-alcoh[...]
hydroxide for four hours, the product was dilut[...]
evaporated until free from methyl alcohol, acidified, [...]
ated, and the mass extracted with ether in a Soxhl[...]
When the ethereal solution was evaporated, a sy[...]
remained, which became partly solid while still on the [...]
This was stirred with concentrated hydrochloric acid, a[...]
powder which separated was collected, washed with [...]
acid, left in contact with porous porcelain in a vacuu[...]
and then analysed :

0·1670 gave 0·2768 CO_2 and 0·0644 H_2O. C=45·7, H [...]
　　$C_9H_{10}O_8$ requires C = 43·9 ; H = 4·0 per cent.

It is obvious that during the hydrolysis under the [...]
tions one molecule of carbon dioxide had been elimina[...]
the above acid is *cyclo*pentane-1 : 2 : 2 : 4-*tetracarbo*[...]

$$CO_2H \cdot CH \bigg\langle {{CH_2 \cdot C(CO_2H)_2} \atop {CH_2 \cdot CH \cdot CO_2H}}$$
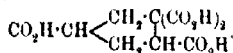
Ethyl cyclo*Pentane*-1 : 2 : 4-*tricarboxylate*, $C_5H_8(CO_2H)$[...]
order to prepare this ester the crude product of the [...]
ethyl *cyclo*pentanepentacarboxylate was heated at 1[...]
hour, when a glassy mass remained, which did not cr[...]
was converted into the ester by heating with alcohol [...]
acid in the usual manner (p. 2670), and the pure subst[...]
at 205—210°/40 mm. :

0·1938 gave 0·4186 CO_2 and 0·1360 H_2O. C = 58·9, H [...]
　　$C_{14}H_{22}O_6$ requires C = 58·7 ; H = 7·8 per cent.

The corresponding trimethyl ester, $C_5H_7(CO_2Me)$ [...]
viously obtained (T., 1900, **77**, 303), and distilled at [...]
12 mm. The pure triethyl ester was hydrolysed wi[...]
alcoholic potassium hydroxide in the usual manner. [...]
removal of the methyl alcohol, acidifying and eva[...]

ness, the mass was extracted with ether in a Soxhlet apparatus. evaporation, the ethereal solution deposited a syrup, which, as rubbed with concentrated hydrochloric acid, crystallised, and solid mass, after washing with hydrochloric acid and drying on was porcelain, melted indefinitely at 115—125°, and was apparently a mixture of the *cis-* and *trans*-modifications of *cyclo*pentane-1 : 4-tricarboxylic acid. In order to demonstrate this, half of the mass was heated with hydrochloric acid in a sealed tube at for four hours. The product was diluted with water, filtered from a small amount of carbonaceous matter, and evaporated to ness; it was then dissolved in water, digested with animal charcoal, and again evaporated. When the syrupy residue was rubbed with concentrated hydrochloric acid, it crystallised with facility (compare T., 1900, **77**, 304), and the solid mass, after washing with porous porcelain and recrystallisation from hydrochloric acid, melted at 129—130°, and consisted of *trans-cyclo*pentane-1 : 2 : 4-tricarboxylic acid :

0·1554 gave 0·2224 CO_2 and 0·0568 H_2O. C = 47·9 ; H = 5·0.

$C_8H_{10}O_6$ requires C = 47·5 ; H = 4·9 per cent.

b. titration 0·1528 neutralised 0·0880 NaOH, whereas this amount of a tribasic acid, $C_8H_{10}O_6$, should neutralise 0·0907 NaOH.

*cyclo***Pentane-1 : 2 : 4-*tricarboxylic Acid*. This modification obtained by heating the crude mixture of acids melting at 5·125° (see above) with acetic anhydride for an hour, and then cling the product, when anhydro-*cis-cyclo*pentanetricarboxylic solidified in the neck of the retort. After recrystallisation from mixture of acetone and chloroform, this substance melted at 5·217°, as stated by Bottomley and Perkin (*loc. cit.*, p. 305). solution of the anhydro-acid in water deposited, on concentration, colourless crystals of *cis-cyclo*pentane-1 : 2 : 4-tricarboxylic acid, ing at 146—148°.

The cis- and trans-cyclo*Hexane-*1 : 2 : 4-*tricarboxylic Acids* (*Hexahydrotrimellitic Acids*).

$$CO_2H \cdot CH \diagdown \genfrac{}{}{0pt}{}{CH_2 \text{———} CH_2}{CH_2 \cdot CH(CO_2H)} \diagup CH \cdot CO_2H.$$

The ethyl butane*tetra*carboxylate,

$$CH(CO_2Et)_2 \cdot CH_2 \cdot CH_2 \cdot CH(CO_2Et)_2,$$
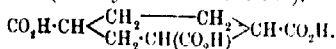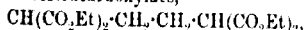
used for these experiments was prepared by the process described by Perkin (T., 1894, **65**, 578). This ester (34·6 grams), dissolved in an equal weight of alcohol, was mixed with a solution sodium (4·6 grams) in alcohol (100 c.c.) and then with ethyl β-bromopropionate (26 grams), when, on setting aside, the

mixture gradually became quite hot. After heating for some time in a soda-water bottle in boiling water, water was added, the ester extracted with ether, and, since it decomposed on distillation, it was at once hydrolysed by boiling with excess of 20 per cent. methyl-alcoholic potassium hydroxide in the usual manner.

Water was then added, the methyl alcohol carefully removed on the water-bath, the product acidified with excess of hydrochloric acid, evaporated to dryness, and extracted in a Soxhlet apparatus with ether.

On evaporation, the ethereal extract deposited a syrup which partly solidified, and this was heated at 190° for half an hour, the syrupy residue being then esterified by boiling with methyl-sulphuric acid and the ester fractionated (compare p. 2673). A cyclohexane-1:2:4-tricarboxylate was thus obtained as a colourless oil, which distilled at about 207°/30 mm.:

0·1898 gave 0·4142 CO$_2$ and 0·1374 H$_2$O.   C = 59·5; H = 8·1

$C_{15}H_{24}O_6$ requires C = 60·0;   H = 8·0 per cent.

This ester was hydrolysed by boiling with excess of 20 per cent. methyl-alcoholic potassium hydroxide for four hours, and, after the methyl alcohol had been completely removed, hydrochloric acid was added, the whole evaporated to dryness, and extracted with ether in a Soxhlet apparatus.

The syrup which remained on distilling off the ether, only partly solidified when it was rubbed with hydrochloric acid, and this had an indefinite melting point, obviously consisting of two or three stereoisomeric modifications. In order to isolate one definite modification (trans-), the whole was heated with concentrated hydrochloric acid in a sealed tube at 190° for four hours, the product was diluted with water, filtered from a small amount of carbonaceous matter, decolorised with animal charcoal, and evaporated to dryness, during which the acid commenced to separate in colourless crystals. After remaining in the ice-chest for two days the crystals were collected, dissolved in ether, filtered from a trace of inorganic matter, and the ether removed, when a solid remained which was crystallised from hydrochloric acid:

0·1786 gave 0·3304 CO$_2$ and 0·0948 H$_2$O.   C = 50·4; H = 5·9

$C_9H_{12}O_6$ requires C = 50·0;   H = 5·6 per cent.

On titration 0·1526 required for neutralisation 0·0840 NaO whereas this amount of a tribasic acid, $C_9H_{12}O_6$, neutralises NaOH.

trans-cycloHexane-1:2:4-tricarboxylic acid is rather sparingly soluble in cold, but readily so in hot water, and has a marked tendency to form supersaturated solutions, which only give

... the acid as a hard, opaque, crystalline crust. It melts at ... 220—221° to a colourless, viscid syrup, but the exact point is ... to observe.

cycloHexane-1:2:4-*tricarboxylic Acid.*—In order to obtain ... acid, the pure *trans*-acid (2 grams) was mixed with acetic ... (5 c.c.) in a test-tube, and gently boiled by means of a ... acid bath for one hour; the temperature was then raised, ... the excess of acetic anhydride distilled off. The test tube was ... cut, and the whole heated as rapidly as possible over a ... flame, when there was much decomposition and a voluminous ... mass remained.

The small quantity of brown distillate, which partly solidified ... was boiled with much water, filtered from a little tar, ... with animal charcoal, and then evaporated to a small ... and mixed with an equal volume of concentrated hydrochloric ... On remaining in the ice-chest a crystalline crust gradually ... and this was collected and crystallised from water, in ... it is rather sparingly soluble in the cold, and from which ... acid separated as a crust of colourless, warty masses, which ... quite different appearance from the crystals of the *trans*

... gave 0·2630 CO_2 and 0·0752 H_2O. C = 50·2; H = 5·8.

$C_9H_{12}O_6$ requires C = 50·0; H = 5·6 per cent.

... titration 0·1405 required 0·0764 NaOH for neutralisation, ... this amount of a tribasic acid, $C_9H_{12}O_6$, neutralises 0·0780 OH

cycloHexane-1:2:4-*tricarboxylic acid* softens at 218°, melts ... and, when it is mixed with an equal amount of the ... modification, the mixture softens very much at 198—200°, ... almost completely melted at 208° (compare p. 2667).

trans-cyclo*Heptane*-1:2:4-*tricarboxylic Acid,*

$$CO_2H\cdot CH {<}^{CH_2-CH_2-CH_2}_{CH_2\cdot CH(CO_2H)}{>}CH\cdot CO_2H.$$
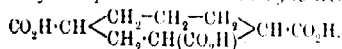
... investigation of this interesting acid has been rendered diffi ... to the small yield which is produced by the following ... and it has not been found possible to obtain better results ... these conditions. Ethyl *cyclo*heptane-1:1:2:4:4-penta ... (p. 2668) was first prepared by mixing 36 grams of ... pentanetetracarboxylate,

$$CH(CO_2Et)_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2$$

... T., 1887, **41**, 240), first with a solution of sodium ethoxide ... by dissolving sodium (4·6 grams) in alcohol (100 c.c.), and

then with ethyl αβ-dibromopropionate (26 grams). And when
initial somewhat vigorous action had subsided, the whole was
in a soda-water bottle in boiling water for four hours. The ester
was isolated by adding water and extracting with ether, and
hydrolysed in the usual manner (p. 2670), the crude dark brown
syrupy polybasic acid being heated at 200° for an hour, and the
residue esterified by boiling with alcohol and sulphuric acid. On
distillation a considerable amount of ethyl pimelate,

$$CO_2Et \cdot [CH_2]_5 \cdot CO_2Et,$$
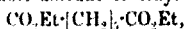
passed over at about 190—195°/100 mm., and then crude ethyl
*cyclo*heptanetricarboxylate distilled at 200—230°/30 mm., leaving
a considerable dark coloured residue in the distilling flask. The
crude tricarboxylic ester was redistilled, and the fraction boiling
at 212—215°/30 mm. analysed, but the yield obtained was only
7 grams, or 8 per cent. of that theoretically possible.

0·1960 gave 0·4390 CO_2 and 0·1504 H_2O. C = 61·1; H =
$C_{16}H_{26}O_6$ requires C = 61·1; H = 8·3 per cent.

This ester was hydrolysed by boiling with methyl-alcoholic
potassium hydroxide in the usual manner, and, after removal of
alcohol, excess of hydrochloric acid was added, the whole evaporated
to dryness, and extracted with ether in a Soxhlet apparatus. The
residue from the ether was a syrup, which could not be made to
crystallise, and was doubtless a mixture of stereoisomerides. It
was heated with hydrochloric acid in a sealed tube at 140° for
four hours, the product diluted with water, filtered from a small
amount of carbonaceous matter, and the hydrochloric acid removed
by evaporation. The residue was dissolved in water, boiled with
animal charcoal, and again evaporated, when a viscid, colourless
syrup was obtained, which, on rubbing, almost completely set.
After contact with porous porcelain, the acid separated from hydro-
chloric acid in hard, nodular masses:

0·1100 gave 0·2106 CO_2 and 0·0623 H_2O. C = 52·2; H = 6·1
$C_{10}H_{14}O_6$ requires C = 52·2; H = 6·1 per cent.

On titration 0·0488 required 0·0250 NaOH for neutralisation,
whereas this amount of a tribasic acid, $C_{10}H_{14}O_6$, should require
0·0254 NaOH.

trans-cyclo*Heptane*-1:2:4-*tricarboxylic acid* melts at 149°
and is readily soluble in water. Unfortunately the amount of
material available was not sufficient for the preparation of the
cis-acid.

THE UNIVERSITY MUSEUM,
OXFORD.

L.—*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part X. The Optical Dispersive Power of Tetrahydro-2-naphthol and its Esters.*

By JOSEPH KENYON and ROBERT HOWSON PICKARD.

...s been shown in Parts VI and IX (this vol., pp. 1117 and ...that the optically active 1-naphthylalkylcarbinols of the ...al formula $C_{10}H_7 \cdot CH(OH) \cdot R$ have complex dispersive powers ... temperatures up to those far removed from their melting ... Thus the methyl member of the series has a complex dis-...ve power at all temperatures up to about 160° and the corre-...ing n-hexyl homologue up to about 180°, above which limiting ...atures the rotations of each obey the law of simple dispersive ... as expressed by the Drude equation with one term, ... It is further of interest to note that in the super-... state at a few degrees below the melting points of these ...ands their temperature-rotation curves for sodium-yellow to ...ry-violet light, which are perfectly regular throughout, exhibit ...n of so-called anomalous dispersion.

...as been suggested (*loc. cit.*) that below these limiting tem-...ures the apparently homogeneous carbinols are really mixtures ... isomerides having rotatory powers of opposite sign, and ...ng in dispersive power. The further suggestion that the ...non is due to a different disposition of the valencies in the ...yl radicle (the two forms being of the nature of *ar-* and ...natives) makes it desirable to consider the dispersive power ... compounds containing either the naphthyl radicle or other ... closely related to it.

...ady in Part III (T., 1912, **101**, 1427) the preparation and ...f the optical properties of both dextro- and lævo-rotatory ...hydro-2-naphthol have been described, but unfortunately ...ied measurements were confined to light of one wave-length ... Accordingly, the work described there has been partly ...ied, and the results confirmed and extended. It has now been ...n that the temperature-rotation curves of *ac*-tetrahydro-2-...ol in the fused state from a temperature of about 120° down ...lting point at 50°, and beyond in the supercooled state to ...out 15°, are perfectly regular and smooth. The rotations ...ed in the homogeneous state up to 120°, as also in various ...ts, obey the law of simple dispersive power, but above 120°

L. CV

FIG. 1.

CHARACTERISTIC DIAGRAM
for
α-Tetrahydro-2-naphthol and some
of its derivatives.

Specific rotatory power.

160°
140°
120°
100°
80°
60°
40°
20°
0°
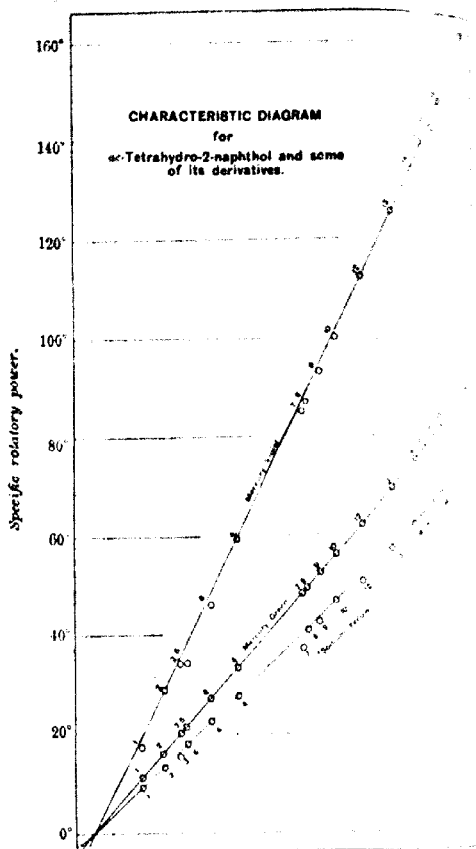
Points marked 1 to 4 correspond with the rotations of the hydrogen ph...
at 5 per cent. concentration in ethyl alcohol, chloroform, pyridine and ...
respectively, points 5 and 6 with ethyl-alcoholic solutions of the sod... ...
potassium salts, points 7, 9 and 10 with the rotations of the valerate ...
homogeneous state at 200°, 100° and 20° respectively, and points 8 and ...
solutions of the valerate in chloroform and carbon disulphide. Points marked ...
to 17 refer to the rotations of the tetrahydronaphthol in the homogeneous state ...
200°, at 140°, dissolved in carbon disulphide and in chloroform, and in ...
homogeneous state at 60° and 20° respectively.   It will be noticed that ...
marked 1, 3, 5, 6, 7 and 12 do not fit on the lines of the diagram.

...ispersive power becomes complex. Of this phenomenon there ... not seem to be any simple explanation, but the properties of ...reduced compound are in marked contrast to those of the ...phthylalkylcarbinols. The *n*-valeric ester in the homogeneous ... at 70° and in solution and the hydrogen phthalate when ...dved in benzene or chloroform also exhibit rotations, which ...ar to conform to the law of simple dispersive power. The ...rate, however, in the homogeneous state at higher temperatures, ...ions of hydrogen phthalate in alcohol or pyridine, and aqueous ...coholic solutions of the sodium or potassium salt of the latter ... all show complex dispersive power.

...he alternative method of plotting such rotations by means of a ...aracteristic diagram " brings out these relations in a striking ...ner. Thus the diagram (Fig. 1), which is constructed in the ...l manner, using the rotations for mercury-green light as a ...rence line, only correlates those rotations of the substances just ...tioned, which conform to the law of simple dispersive power. ... not surprising that the diagram fails to correlate the rotations ...he valerate in the homogeneous state at higher temperatures, ...not only has the *ac*-tetrahydro-2-naphthol then a complex dis...ire power, but also, as has been repeatedly shown, an esterified ...cylic group exhibits complex dispersive power at high tem...tures. Assuming that dynamic isomerism is the underlying ...e of the complex dispersive power exhibited by a colourless ...pound of simple chemical constitution (containing only one ...metric carbon atom), it may be stated generally that in cases ...e complex dispersive power is exhibited at all temperatures the ...pound will contain more than one possible centre of dynamic ...erism. Illustrations of this general statement can be seen in ...esters of the naphthylalkylcarbinols and of *ac*-tetrahydro-2-...thol, whilst each of the substances mentioned above as showing ...let dispersive power when dissolved in certain solvents con...s when so dissolved, two possible centres of dynamic isomerism, ...the observed rotations cannot be correlated on the characteristic ...am (Fig. 1). However, the rotations shown by aqueous solu...at various concentrations of sodium *ac*-tetrahydro-2-naphthyl ...late can be correlated on another diagram (Fig. 2) specially ...for these, and permit the inference that there is some relation ...ween them.

...tention has already been drawn in this series of investigations ...e danger of basing conclusions on the values of any one disper...ratio. A good example of this danger is to be seen in the ...sion ratios of the substances named in tables I and II. It ...be noted that in the homogeneous state the ratio for mercury-

8 M 2

violet/green remains constant, but that for mercury-violet and
yellow tends constantly to increase.   This is well brought out in
the diagram (Fig. 1), where the lines for violet, green and yellow

FIG. 2.

CHARACTERISTIC DIAGRAM
for
Sodium *l-a*-tetrahydro-2-naphthyl
phthalate in aqueous solutions.
(1) 2 0 per cent. solution
(2) 4 2   „   „
(3) 6 1   „   „
(4) 8 0   „   „
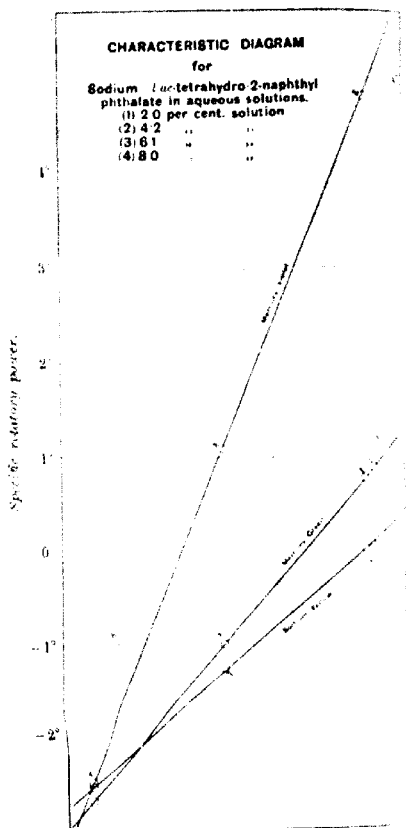
intersect at zero.   When the green is used as a reference line, the
rotation values for violet and green all lie approximately in
two lines, so that the dispersion ratio is constant, but in the case
where complex dispersive power (see, for example, points and

TABLE 1

Rotatory Powers at Different Temperatures.

d-ac-Tetrahydro-2-naphthol.

Temp.	Density D .	$[\alpha]_A$	$[\alpha]_{Li}$	$[\alpha]_{Na}$	$[M]_{Li}$	$[M]_{Na}$	$[M]_{Hg}$	Dispersion ratios.	
					$+112.0°$	$+133.6°$	$+240.0°$	Mercury violet.	Hg violet Na yellow.
20°	1.0910	+75.68	+90.26	+162.16	+112.0	+133.6	+240.0	1.797	2.142
40	1.0750	71.85	88.72	155.51	106.4	128.3	230.2	1.793	2.164
60	1.0590	68.35	82.62	148.94	101.2	122.3	220.5	1.793	2.179
80	1.0431	65.36	79.16	142.05	96.7	117.1	210.3	1.796	2.174
100	1.0275	62.56	75.30	135.65	92.8	111.6	200.8	1.799	2.169
120	1.0121	59.94	72.33	130.13	88.7	107.0	192.6	1.799	2.171
140	0.9965	57.50	69.82	125.88	85.1	103.4	186.3	1.803	2.190
160	0.9790	55.26	67.36	121.04	81.8	99.7	179.2	1.797	2.191
180	0.9630	52.96	64.66	116.10	78.4	95.7	171.9	1.796	2.193
200	0.9470	50.86	62.47	112.15	75.3	92.5	166.0	1.793	2.205

l-ac-Tetrahydro-2-naphthyl n-Valerate.

Temp.	Density D .	$[\alpha]_A$	$[\alpha]_{Li}$	$[\alpha]_{Na}$	$[M]_{Li}$	$[M]_{Na}$	$[M]_{Hg}$	Dispersion ratios.	
20	1.0284	-46.80	-56.25	-99.97	-108.6	-130.5	-231.9	1.774	2.135
40	1.0140	45.77	55.54	98.40	106.2	128.3	226.7	1.775	2.134
60	0.9995	44.71	54.48	96.74	103.7	126.3	224.5	1.775	2.165
80	0.9853	43.24	53.60	95.18	101.2	124.7	220.7	1.775	2.181
100	0.9709	41.59	51.54	93.40	98.6	121.8	216.6	1.775	2.199
120	0.9565	40.62	50.56	91.60	95.9	119.4	212.4	1.776	2.216
140	0.9421	39.63	48.56	89.80	92.9	117.5	209.4	1.775	2.234
160	0.9276	38.78	47.55	87.96	90.0	114.9	204.1	1.776	2.268
180	0.9133	36.43	45.45	85.96	86.8	112.4	199.5	1.774	2.297

TABLE II.

d-ac-Tetrahydro-2-naphthol.

Solvent	Length of observation tube, cm.	Weight of substance dissolved, grams.	$a_{..}$	$a_{..}$	$a_{..}$	$[a]_{..}$	$[a]_{..}$	$[a]_{..}$	$[a]_{..}$	$[M]_{..}$	$[M]_{..}$	$[M]_{..}$	$[M]_{..}$	Dispersion ratios. Hg violet	Hg green	Mercury : Sodium yellow
Pyridine	22	1·0163	+8·49°	+10·23°	+18·40°	+75·97°	+91·54°	+164·6°	+112·4°	+135·5°	+243·6°	1·799	2·167			
Ethyl alcohol	20	1·0313	7·78	9·37	16·03	75·56	90·88	161·4	111·9	134·5	238·8	1·775	2·135			
Chloroform ...	22	0·9968	7·98	8·85	15·70	67·32	80·71	143·2	99·63	119·5	211·9	1·774	2·127			
Carbon disulphide..	20	1·0206	6·36	7·67	13·71	82·30	75·13	134·3	92·21	111·2	198·7	1·787	2·155			
Benzene	20	0·9653	5·95	7·14	12·70	61·50	73·98	131·6	91·24	104·5	194·7	1·778	2·134			

d-ac-Tetrahydro-2-naphthyl Hydrogen Phthalate.

| Chloroform ... | 22 | 1·0718 | +1·60 | +1·89 | +3·40 | +13·57 | +16·03 | +28·84 | +40·17 | +47·44 | +85·37 | 1·799 | 2·125 | | | |

Brucine Salt of the d-Ester.

| Ethyl alcohol | 22 | 1·0621 | +0·48 | +0·25 | −1·05 | +4·11 | +2·14 | −8·99 | +29·35 | +14·77 | −62·03 | — | — | | | |

l-ac-Tetrahydro-2-naphthyl Hydrogen Phthalate.

Ethyl alcohol	22	0·9830	−1·05	−1·22	−1·85	−9·72	−11·28	−17·11	−28·74	−33·39	−50·64	1·517	1·762			
Chloroform ...	22	1·0212	1·54	1·04	3·31	13·71	17·27	29·40	40·58	51·12	87·02	1·706	2·149			
Pyridine	22	1·0597	1·85	2·33	3·90	15·87	19·00	34·43	46·98	59·17	101·9	1·712	2·155			
Benzene	22	0·4423	1·34	1·02	2·90	27·54	33·30	5·61	51·63	98·56	176·4	1·780	2·144			

Conchairamine Salt of the l-Ester.

| Ethyl alcohol | 22 | 1·1052 | 1·51 | 11·01 | 19·72 | 72·40 | 80·74 | 102·20 | 214·5 | 208·0 | 480·1 | 1·788 | 2·230 | | | |

TABLE III.

Sodium l-ac-Tetrahydro-2-naphthyl Phthalate.

Solvent.	Length of observation tube, cm.	Weight of solute, grams.	a_v°	a_r°	a_i°	$[a]_v$°	$[a]_r$°	$[a]_i$°	$[M]_v$°	$[M]_{r-v}$°	$[M]_{i-r}$°
Water	22	0·5117	±0°	+0·04°	+0·26°	±0°	+0·87°	+5·63°	±0°	+2·77°	+17·96°
"	22	1·0332	±0	+·07	+0·45	±0	+0·75	+4·84	±0	+2·40	+15·39
"	22	1·5280	−0·17	−·14	+0·15	−1·24	−1·02	+1·10	−3·93	−3·24	+3·47
"	22	1·9660	−0·45	−·48	+0·44	−2·54	−2·71	−2·49	−8·09	8·53	+7·82
Ethyl alcohol	22	0·9423	−1·53	−1·83	−2·91	−18·05	−21·69	−34·26	−57·40	−68·66	−108·9

1-a-Tetrahydro-2-naphthyl n-Valerate.

Solvent.	Length of observation tube, cm.	Weight of solute, grams.	a_v°	a_r°	a_i°	$[a]_v$°	$[a]_r$°	$[a]_i$°	$[M]_v$°	$[M]_{r-v}$°	$[M]_{i-r}$°
Chloroform	22	0·9867	−4·45	−5·38	−9·48	−41·01	−49·57	−87·34	−95·13	−115·0	−202·6
Ethyl alcohol	20	1·0087	−4·15	−4·98	−5·91	−41·21	−49·45	−88·49	−95·61	−114·8	−205·3
Benzene	20	0·8279	−4·44	−5·35	−9·53	−53·63	−64·63	−116·1	−124·5	−149·9	−267·1
Carbon disulphide	20	1·0292	−6·57	−7·96	−14·40	−63·86	−77·36	−140·0	−148·1	−179·5	−324·7

7 and 12) is exhibited the rotations for sodium-yellow light ... fall on the line so that the ratio violet/yellow is not const...

EXPERIMENTAL.*

ac-Tetrahydro-2-naphthol.

The preparation of this compound from β-naphthol by Bamberger and Lodter's method (*Ber.*, 1880, **23**, 205) gives only poor ... One cause of this is the loss occasioned when the ethereal s... of the reduced naphthol is washed repeatedly with the warm solution of sodium diazobenzenesulphonate to remove the ... sponding *ar*-compound. This operation, however, can be ... and the product converted into hydrogen phthalic ester. ... sodium salt of the hydrogen phthalate of *dl-ac*-tetrahydr... crystallises with great readiness from water, and its prepar... affords a much better method of purifying the *ac*-compound... the older one.

This *sodium* salt crystallises from water in long needles ... aqueous alcohol in large tablets, has the composition

$$CO_2Na \cdot C_6H_4 \cdot CO_2 \cdot C_{10}H_{11}, 4H_2O,$$
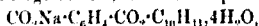
effloresces at about 60°, does not melt below 200°, and ... soluble in ethyl alcohol:

0·3218 lost 0·0582 H_2O and gave 0·0584 Na_2SO_4. H_2O ...
Na = 5·88.

$C_{18}H_{15}O_4Na, 4H_2O$ requires $H_2O = 18·23$; Na = 5·88 per cent.

The resolution of the *dl*-hydrogen phthalate was carried ... the manner already described (*loc. cit.*), and the results were ... firmed. The *d*- and *l*-esters form *sodium* salts, which have ... properties to that of the *dl*-ester.

Determinations of Rotatory Power ($\alpha^{100 \text{ mm.}}$) *of the Ca*... l-ac-*Tetrahydro-2-naphthyl* n-*Valerate in the Homogeneous* ...

d-ac-Tetrahydro-2-naphthol.

Temp.	28·5°	65°					
α_D	+80·50°	71·20°	(see also Part III., *loc. cit.*).				

Temp.	27°	59°	82°	126°	136°	156	..
α_{gr} ...	+96·72°	88·54°	82·00°	71·72	70·58°	66·88	1·2

Temp.	26·5°	58°	84°	126°	137°	157	..
α_{vi}	+173·60°	158·80°	140·04°	129·64°	126·30°	119·70	1..

* When not otherwise stated, the experimental procedure is similar ... previously described (*loc. cit.*).

l-ac-*Tetrahydro-2-naphthyl* n-*Valerate.*[*]

	20°	44°	54°	110°	135	161°
α	−48·12°	46·24°	45·64°	40·16°	38·36	35·80°
	20°	43°	59°	110°	138	160
α	−57·80°	55·86°	54·44°	50·22°	47·84	−46·00°
	20°	41°	59°	110°	136	162°
α	−102·78°	−99·90°	−96·52°	−89·60°	85·00	81·20°

11.—*The Reduction Products of Ethyl Hydrindene-2:2-dicarboxylate.*

By JAMES KENNER.

In a previous communication it was suggested that the ease with which cyclic condensation occurs should be modified by the presence in the chain of certain carbon atoms which, being already members of a closed ring, have the directions of their valencies to some extent determined (Kenner and Turner, T., 1911, **99**, 2102). The investigation now to be described was undertaken with the object of studying ring-formation from compounds, the molecules of which contain one carbon atom fulfilling this condition; in other words, the preparation of *spiro*-compounds was to be attempted.

As substituent groups are also known to be important factors in determining the facility of formation, and stability, of cyclic compounds it appeared that, among *spiro* compounds, the hydro-carbons would furnish the most decisive evidence of the influences referred to in the preceding paragraph. These and other considera-tions suggested the application to ethyl hydrindene 2:2 dicarboxyl-ate of Bouveault and Blanc's method of reduction by means of

[*] These rotations are somewhat lower than those previously published. It has been thought necessary to investigate the cause of the discrepancy, as this paper deals with optical dispersive power, which is only very slightly affected by the discrepancy.

sodium and ethyl alcohol, in the hope of preparing aa'-dihydro-2 : 2-dimethylhydrindene (I), from which the hydrocarbon

$$C_6H_4\!<\!\!{}^{CH_2}_{CH_2}\!\!>\!C\!<\!\!{}^{CO_2Et}_{CO_2Et} \rightarrow C_6H_4\!<\!\!{}^{CH_2}_{CH_2}\!\!>\!C\!<\!\!{}^{CH_2\cdot OH}_{CH_2\cdot OH} \rightarrow$$
$$\text{(I.)}$$

$$C_6H_4\!<\!\!{}^{CH_2}_{CH_2}\!\!>\!C\!<$$
$$\text{(II.)}$$
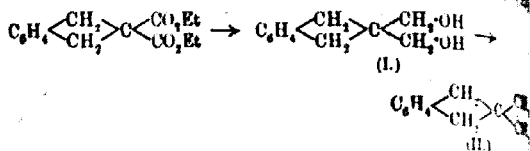
might subsequently be obtained.

It had previously been shown by Bouveault and Blanc that *iso*diisobutylmalonate, whilst furnishing a certain amount of the expected glycol, was to a considerable extent decomposed in the following way under the influence of sodium ethoxide formed during the reaction :

$$(C_4H_9)_2C(CO_2Et)_2 + C_2H_5\cdot OH \longrightarrow (C_4H_9)_2CH\cdot CO_2Et + CO_2Et_2$$

the ethyl *iso*valerate being then reduced in the normal manner (*Bull. Soc. chim.*, 1904, [iii], **31**, 1203). Ethyl hydrindenedioxylate had, however, been shown by Thole and Thorpe to be quite stable towards sodium ethoxide at the ordinary temperature (T., 1911, **99**, 2186), and the hope was therefore entertained that even at the higher temperature to be used in these experiments the type of decomposition observed by Bouveault and Blanc might not assert itself in a marked degree. This expectation, however, was not realised, for the yield of the glycol (I) was disappointingly small, being less than 3 per cent. of the calculated. More than 40 per cent. of the ethyl hydrindenedicarboxylate was converted into 2-*hydroxymethylhydrindene* (III), the remainder being recovered in the form of a mixture of hydrindene-mono- and -dicarboxylic acids, in which the former largely predominated

$$C_6H_4\!<\!\!{}^{CH_2}_{CH_2}\!\!>\!CH\cdot CH_2\cdot OH.$$
$$\text{(III.)}$$
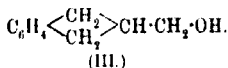
Initially, therefore, the dicarboxylic ester was almost entirely converted into the monocarboxylic ester, and, in the author's opinion, this reaction must be ascribed to spatial causes, as will be discussed later. It is probable that such influences also play a part, although possibly a subordinate one, in promoting the decompositions discussed by Thole and Thorpe (*loc. cit.*).

2-Hydroxymethylhydrindene was readily converted by the usual means into 2-*bromomethylhydrindene* (IV), the reactions of the

$$C_6H_4\!<\!\!{}^{CH_2}_{CH_2}\!\!>\!CH\cdot CH_2Br \qquad\qquad CH_3\cdot CH\!<\!\!{}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}\!\!>\!CH\cdot R$$
$$\text{(IV.)} \qquad\qquad\qquad\qquad\qquad \text{(V.)}$$
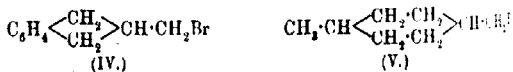
rited investigation, because it has frequently been observed that
a bromine atom in derivatives of this type is remarkably inert.
As Perkin and Pope found that 1-methyl-4-bromomethyl*cyclo-
hexane* (V) was converted into the cyanide only with considerable
dificulty (T., 1908, **93**, 1079). Similar relationships were dis-
rared in the present instance. The bromo-compound was un-
affected after prolonged boiling with amalgamated zinc and hydro-
benz acid, in spite of the efficiency of this reducing agent (Clem-
mensen, *Ber.*, 1913, **46**, 1837; 1914, **47**, 51, 681). Interaction of
, bromo-compound and ethyl sodiomalonate in alcoholic solution
for ten hours at the boiling point resulted in the production of
to about 65 per cent. of the calculated amount of *ethyl 2-hydrin-
methylmalonate* (VI):

$$H_4 \diagup{CH_2}\diagdown{CH_2} \diagup CH \cdot CH_2 Br + CHNa(CO_2Et)_2 \longrightarrow$$

$$C_6H_4 \diagup{CH_2}\diagdown{CH_2} \diagup CH \cdot CH_2 \cdot CH(CO_2Et)_2$$
$$(VI.)$$
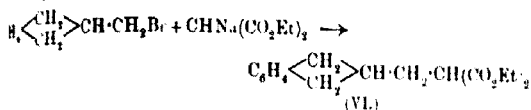
The formation of 2-*phthaliminomethylhydrindene* (VII) by heat-
ing the bromo-derivative with potassium phthalimide at 180—200°
for some hours was similarly incomplete:

$$H_4 \diagup{CH_2}\diagdown{CH_2} \diagup CH \cdot CH_2 Br + C_6H_4 \diagup{CO}\diagdown{CO} \diagup NK \longrightarrow$$

$$C_6H_4 \diagup{CH_2}\diagdown{CH_2} \diagup CH \cdot CH_2 \cdot N \diagup{CO}\diagdown{CO} \diagup C_6H_4$$
$$(VII.)$$
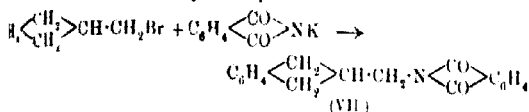
The contrast between the inertia of the bromine atom in such
compounds and its activity in, for instance, benzyl bromide, is
worthy of some comment, and is obviously in some way connected
with the difference between the saturated and the unsaturated
conditions of the cyclic structures present in the two types of
compounds. If, however, benzyl bromide be represented by the
formula (VIII), in Flürscheim's notation, it would appear to follow
as a striking consequence that Perkin and Pope's 1-methyl-4-bromo-
methyl*cyclo*hexane is to be represented by the formula IX :

$$\diagdown{-CH_2-Br}$$
$$(VIII.)$$

$$CH_3 \cdot CH \diagup{CH_2 \cdot CH_2}\diagdown{CH_2 \cdot CH_2} \diagup CH - CH_2 - Br$$
$$(IX).$$
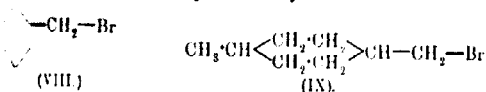
The similar inertia of the bromine atoms in tetrabromotetra-
methylmethane (Perkin and Simonsen, T., 1905, **87**, 161; Fecht,
ibid., 1907, **40**, 3884) would then find expression in the formula X :

$$\begin{matrix} Br-CH_2 \\ Br-CH_2 \end{matrix} \diagup C \diagdown \begin{matrix} CH_2-Br \\ CH_2-Br \end{matrix}$$
$$(X.)$$
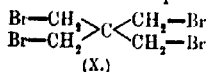
The facts symbolised by these formulæ are illustrative of the influences referred to at the commencement of this paper, and in the author's opinion, they are all explicable by a thorough application of Baeyer's strain theory. For it is at once clear that the normal relative positions of substituents known to exert steric hindrance, such as methyl (or bromomethyl) and carboxyl groups, may, when they are attached to the same carbon atom, be comparable, in regard to this atom, with those of the carbon atoms of, for instance, a *cyclo*hexane or a *cyclo*heptane ring. Then, adopting Werner's conception of the uniform spherical distribution of affinity round a carbon atom ("Beiträge zur Theorie der Affinität und Valenz," Zurich, 1891), we see that, if *aa'* in XI represent a section the zones of affinity appropriated by two univalent groupings in the plane of the paper when "the angle between two valencies is 109°28'," an increase in this angle will cause an alteration in the relative position of the zones, which will now be represented by XII:

(XI.)   (XII.)
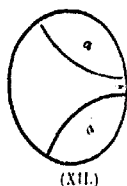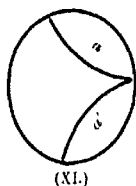
In this manner a certain amount of affinity, corresponding to the region (*b*), will be left unsatisfied, and the extent of this region is a measure of the "strain," in Baeyer's terminology. If the two groups attached to the carbon atoms be free to move, they will probably so adjust themselves as partly to engage the valency left free because the change in position of the zones *aa'* makes an incursion into the zones of affinity previously available for them.

In the following paragraphs, the attempt is made to apply these considerations to the cases in which (*a*) two of the groups attached to a carbon atom are components of the same cyclic system, whilst the other two are groups of large molecular volume. In these cases the motion of the former groups is restricted, and the affinity represented by *b* will then remain free and available to a greater or less extent as partial valency to an atom situated above or below the plane of the paper and, for example, coplanar with the atoms appropriating *aa'*.

Thus, in the case of ethyl hydrindenedicarboxylate there will be residual affinity on the quaternary carbon atom, and, owing to the encroachment of the carbethoxy-groups on the zones of affinity

ually available for the two carbon atoms of the hydrindene ring,
... more of these groups will obtain less than its proper share
...inity. This deduction is in agreement with the experimental
...nce just advanced, according to which we may conclude that
...ster is more adequately represented by the formula XIII:

$$C_6H_4{<}^{CH_2}_{CH_2}{>}C{<}^{CO_2Et}_{CO_2Et}$$

(XIV.)
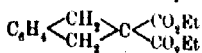
...ular considerations probably supply an explanation of a
...ber of reactions met with in the chemistry of cyclic compounds.
...lustration of this may be cited the change of carone into
...retone by distillation (Baeyer, *Ber.*, 1894, **27**, 1917), and into
... and hydroxy-menthanone by absorption of the elements
...ydrogen bromide or water (*ibid.*, p 1920); the isomerisation
...arylamine hydrochloride into vestrylamine hydrochloride
...*yer. Ber.*, 1894, **27**, 3486); the disruption of the bridge
...methyldicyclopentanonecarboxylic acid by reduction (Perkin,
...ye. and Walker, **T.**, 1901, **79**, 729); the addition of the
...ents of hydrogen bromide to α-camphylic acid (Perkin, T.,
... **83**, 842); and the various reactions by which the bridge in
...amphor molecule is broken between two quaternary carbon
...s (see Aschan, "Konstitution des Kamphers," Braunschweig,
...3, p. 79).

...he reactions of certain other compounds are illustrative of
...ther mode of relieving the stress on the quaternary carbon atom,
...ely, the replacement of two single bonds by a double bond.
...s results in a smaller demand being made on the affinity of the
...nal carbon atom. Thus Wallach has shown that ethyl *cyclo-
...hol-1-acetate* on hydrolysis is partly converted into *cyclo-
...anone*, accompanied by some *cyclo*hexanol (a hydrogen atom
...ng displaced a group of large molecular volume). Further,
...hydration of the ester or of the acid is easily carried out, and
...lts in the formation of Δ¹-*cyclo*hexeneacetic acid or of carboxy-
...ylene*cyclo*hexane, according to the agent employed. Indeed,
...nitial condensation product of 1:5-dimethyl-Δ¹-*cyclo*hexen-3-
...cannot be isolated, but passes over at once into 1:5-dimethyl-
...cyclo*hexadienyl-3-acetic acid (*Annalen*, 1900, **314**, 147; 1902,
...135; 1905, **343**, 40, **347**, 316; 1908, **360**, 26). That these
...tions are not due to the presence of the hydroxyl group as
...is shown by a remarkable instance of an analogous kind, com-
...icated to the author by Prof. J. F. Thorpe. Ethyl *cyclo-
...ne-αα'-dibromodiacetate* (XIV) when boiled with dilute potass-
...m hydroxide solution is converted into carboxymethylene*cyclo-*

hexane (XV), although when it is dropped into concentrated aqueous potassium hydroxide at 130° the acid (XVI) is produced

$$CH_3 \diagdown \!\!\!\! \begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} \!\!\!\! \diagup C \diagdown \!\!\!\! \begin{matrix} CHBr \cdot CO_2Et \\ CHBr \cdot CO_2Et \end{matrix} \rightarrow$$

(XIV.)

$$CH_3 \diagdown \!\!\!\! \begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} \!\!\!\! \diagup C{:}CH \cdot CO_2H \; ; \quad CH_3 \diagdown \!\!\!\! \begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} \!\!\!\! \diagup C \diagdown \!\!\!\! \begin{matrix} C(OH){:}O_2H \\ CH \cdot CO_2H \end{matrix}$$
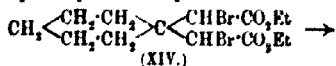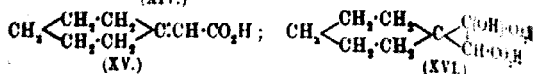
(XV.)   (XVI.)

It is obvious that similar conditions will prevail when, as in the instances quoted above, three or four separate groups of large molecular volume are attached to a single carbon atom.

When, as in the molecule of *cyclo*propane-1 : 1-dicarboxylic acid the cyclic structure is such that the "angle between two valencies of the quaternary carbon atom is less than 109°28′, the effect just discussed will be intensified. Hence this acid and 1 : 1-methyl*cyclo*propane are almost comparable with unsaturated compounds in the readiness with which they take part in additive reactions, and the general conclusions of Kötz (*J. pr. Chem.*, 1903, [ii], **68**, 174) in regard to the derivatives of *cyclo*propane are in agreement with the statement just made. Further Radulescu's observation that the acid (XVII) is stable toward halogen hydrides (*Ber.*, 1909, **42**, 2771; 1911, **44**,) appears to be direct evidence in favour of the suggestion that the carbonyl groups are differently situated with regard to the central carbon atom from those in *cyclo*propane-1 : 1-dicarboxylic acid.

$$\begin{matrix} CH_2 \\ CH_2 \end{matrix} \!\!\!\! \diagup C \diagdown \!\!\!\! \begin{matrix} CO \cdot CH \cdot CO_2H \\ CO \cdot CH \cdot CO_2H \end{matrix}$$
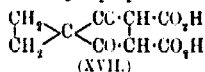
(XVII.)

The rearrangement of derivatives of ethylene oxide into those of acetaldehyde are instances of a similar nature among hetero cyclic compounds (Fourneau and Tiffeneau, *Compt. rend.*, 1905, **141**, 662; Klages, *Ber.*, 1905, **38**, 1969; Klages and Kessler, *Ber.*, 1906, **39**, 1753):

$$\begin{matrix} CPh_2 \\ CH_2 \end{matrix} \!\!\!\! \diagup O \rightarrow \begin{matrix} CHPh_2 \\ CHO \end{matrix} \; ; \quad \begin{matrix} CPhMe \\ CH_2 \end{matrix} \!\!\!\! \diagup O \rightarrow \begin{matrix} CHPhMe \\ CHO \end{matrix}$$
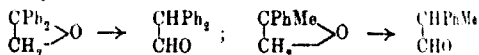
Both pairs of valencies attached to the carbon atom that is inclined to one another at angles less than 109°28′, when some instability of the molecule may be expected. Thus the following table shows in the case of the central carbon atom of the open compound, $(CH_2)_xC(CH_2)_y$, the angle between a valency of the $(x+1)$-membered ring and one of the $(y+1)$-membered ring:

		$y+1$	
$x+1$	2	3	4
2	180	150′	135°
3		139	128

magnitude of these angles indicates that considerable
amts of unsatisfied affinity will exist between the zones corre-
ding with the valencies in question. Consequently, compounds
as type may be very difficult to isolate, and, when obtained,
liable to undergo change. Thus Dimroth and Feuchter were
le to prepare an allene derivative from the compounds XVIII
XIX (*Ber.*, 1903, **36**, 2238; compare Ipatiev, *J. pr. Chem.*,
[ii], **59**, 517):

$$\frac{C_2H_5}{CO_2Et}{>}C{:}CCl{\cdot}CH_2{\cdot}CH_3 \qquad \frac{C_2H_5}{CO_2Et}{>}CH{\cdot}CC{:}CH{\cdot}CH_3$$

(XVIII.)   (XIX.)
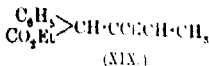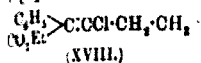
arly, ethyl allenetetracarboxylate (XX), which is only
med by heating the initial product (XXI) of the action of
sodiomalonate on carbon tetrachloride, absorbs two molecular
rtions of water when exposed in a moist atmosphere (Zelinski
Doroschevski, *Ber.*, 1894, **27**, 3376):

$$+ 2Na_2C(CO_2Et)_2 + C_2H_5{\cdot}OH \;\rightarrow\; CH{<}^{C(CO_2Et)_2}_{C(OEt)(CO_2Et)} \;\rightarrow$$

(XXI.)

$$C{\ll}^{C(CO_2Et)_2}_{C(CO_2Et)_2}$$

(XX.)
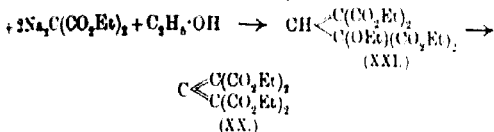
e action of alcoholic potassium hydroxide on iodomethyl*cyclo*-
ane leads to the production of erythrene, presumably owing to
earrangement of methylene*cyclo*propane (Demjanov, *J. Russ.
Chem. Soc.*, 1903, **35**, 375):

$$\frac{CH_2}{CH_2}{>}CH{\cdot}CH_2I \;\rightarrow\; \left[\frac{CH_2}{CH_2}{>}C{:}CH_2\right] \;\rightarrow\; \frac{CH}{CH_2}{\diagdown}CH{:}CH_2.$$
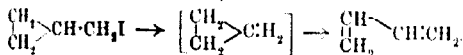
w, Favorski and Batalin have recently shown (*Ber.*, 1914,
1648) that Gustavson was mistaken in attributing the consti-
a of an ethylidene*cyclo*propane to a compound he had prepared
analogous manner (*Compt. rend.*, 1896, **123**, 242). Further,
cle product of dehydration of *cyclo*propyldimethylcarbinol is
*iso*propyl*iso*propylene (XXII), notwithstanding the fact that

$$OH{\cdot}C(CH_3)_2{\cdot}CH{<}^{CH_2}_{CH_2} \;\rightarrow\; CH_2{:}C(CH_3){\cdot}CH{<}^{CH_2}_{CH_2}$$
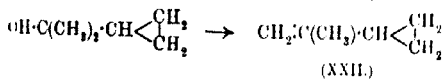
(XXII.)

hyl*iso*propylcarbinol furnished the isomeric olefines (XXIII
XXIV) in the proportion of three to one (Henry, *Compt. rend.*,
147, 557):

$$(CH_3)_2{\cdot}CH(CH_3)_2 \;\rightarrow\; C(CH_3)_2{:}C(CH_3)_2 \quad \text{and}$$

(XXIII.)

$$CH_2{:}C(CH_3){\cdot}CH(CH_3)_2.$$

(XXIV.)
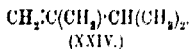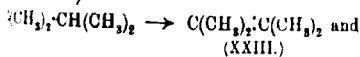
The production of methylene*cyclo*butane (XXV), in spiro*pentane (XXVI), from tetrabromotetramethyl_____ doubtless to be ascribed to similar causes (Demjanov, *Ber.* 41, 915; Favorski and Batalin, *loc. cit.*; compare G_____ and Bulatov, *J. pr. Chem.*, 1896, [ii], 54, 97; 56, 93, *Ber. loc. cit.*; Zelinski, *Ber.*, 1913, 46, 170):

$$\begin{array}{c} CH_2Br \\ CH_2Br \end{array}\!\!>\!C\!<\!\!\begin{array}{c} CH_2Br \\ CH_2Br \end{array} \rightarrow \begin{array}{c} CH_2 \cdot C\!:\!CH_2 \\ CH_2 \cdot CH_2 \end{array}; \begin{array}{c} CH_2 \\ CH_2 \end{array}\!\!>\!C\!<\!\!\begin{array}{c} CH \\ CH \end{array}$$
$$\text{(XXV.)} \qquad\qquad \text{(XXVI)}$$
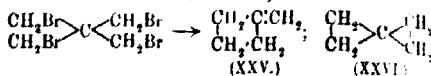
Neither this hydrocarbon nor *cyclo*butanone (Kishner, *J. Phys. Chem. Soc.*, 1905, 37, 106; 1907, 39, 922) exhibits tendency towards the breaking down of the four-membered but it is significant that *cyclo*butane-1:3-dione behaves as it were represented by the formula XXVII (Chick and W. T., 1910, 97, 1982):

$$\begin{array}{c} CH_2 \cdot C\!\!<\!\!^{O} \\ | \\ O\!:\!C \cdot CH_2\!\!- \end{array}$$
$$\text{(XXVII.)}$$
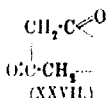
The illustrations thus brought forward are not intended exhaustive, but suffice to indicate the aspect from which author's opinion, the study of *spiro*-compounds sho approached. The quaternary carbon atom is not *per se* of weakness, this being conditioned by the distortion of its from their normal positions.

Finally, it may be mentioned that experiments have als initiated with a view, on the one hand, to the synthesis compound (XXVIII) by the condensation of the chloride of dene-2:2-dicarboxylic acid with benzene, and, on the other

$$C_6H_4\!\!<\!\!\begin{array}{c} CH_2 \\ CH_2 \end{array}\!\!>\!C\!<\!\!\begin{array}{c} COCl \\ COCl \end{array} + C_6H_6 \rightarrow C_6H_4\!\!<\!\!\begin{array}{c} CH_2 \\ CH_2 \end{array}\!\!>\!C\!<\!\!\begin{array}{c} CO \\ CO \end{array}\!\!>\!\!$$
$$\text{(XXVIII.)}$$
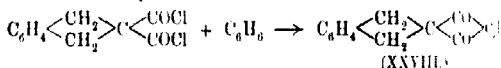
preparation of reduction products of ethyl *cyclo*hexane____ from which *spiro*-compounds might be prepared. The investi in this direction has, however, only just been commenced, a measure of success attained is indicated in the experimental p of this paper.

EXPERIMENTAL.

Reduction of Ethyl Hydrindene-2:2-dicarboxylate

Sodium (30 grams), cut into pieces the size of a pea, was in a large flask, fitted with a long, upright condenser and funnel, and the flask was heated to 80° in an oil-bath. A

absolute alcohol of ethyl hydrindenedicarboxylate (23 grams), newly purified by distillation under diminished pressure c.c.), was then run from the tap-funnel on to the sodium as far as possible, consistent with efficient action of the condenser. temperature of the oil-bath was then raised to 130°, and a fresh quantity of alcohol (100 c.c.) gradually added in the course so hours. At the end of five hours from the experiment any formed ester was hydrolysed by the gradual addition of water to mixture. The product was then cooled, considerably diluted, treated with sufficient sulphuric acid to leave the solution only alkaline. By exhaustive extraction with ether the mixture reaction products was removed, whilst hydrindenemonocarb- acid (5·5 grams) could be recovered by subsequent acidifica- of the aqueous solution.

ethereal extracts, after treatment in the usual manner, an oil, which was distilled under diminished pressure. manner a large fraction (5·5 grams) was obtained, which at about 140°/11 mm. and solidified at the ordinary tem- ure.

hydroxymethylhydrindene (III), obtained in this way, has a characteristic agreeable odour, and consists of prismatic crystals, melt at 33° and boil at 139—140°/11 mm. It is readily in most organic solvents, but only sparingly so in light eum (b. p. 40—50°), and may be crystallised from this

gave 0·4424 CO_2 and 0·1078 H_2O. C = 80·98; H = 8·04.

$C_{10}H_{12}O$ requires C = 81·07; H = 8·11 per cent.

phenylurethane, $C_6H_4 {\small\begin{matrix} CH_2 \\ CH_2 \end{matrix}} CH \cdot CH_2 \cdot O \cdot CO \cdot NH \cdot C_6H_5$, was

ed by heating a solution of molecular proportions of the and phenylcarbimide in light petroleum (b. p. 90—110°). crystallisation, it melted at 99·5°:

gave 10·2 c.c. N_2 at 11° and 755 mm. N = 5·59.

$C_{17}H_{17}O_2N$ requires N = 5·24 per cent.

hydroxy-2:2-dimethylhydrindene (I) was obtained by dis- the united residues from four of the above preparations of oxymethylhydrindene. A colourless oil passed over at about mm., and rapidly solidified. On the addition of light eum (b. p. 90—110°) to its solution in ethyl alcohol, small, nal prisms, melting at 112·5°, separated. The yield was

gave 0·4266 CO_2 and 0·1090 H_2O. C = 74·20; H = 7·73.

$C_{11}H_{14}O_2$ requires C = 74·16; H = 7·86 per cent.

Reduction of Ethyl Hydrindene-2-carboxylate.

A solution of the ester (20 grams) in alcohol (100 c.c.) was added to sodium (18 grams) in precisely the same manner as that described for the previous case, alcohol (20 c.c.) being subsequently added. The yield of carbinol was 8·5 grams.

2-Aldehydohydrindene, $C_6H_4\underset{CH_2}{\overset{CH_2}{<}}>CH\cdot CHO.$
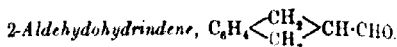
2-Hydroxymethylhydrindene (10 grams), having been added to a solution of chromic acid (4·2 grams) in 10 per cent. sulphuric acid (75 grams), the mixture was heated on the water-bath for two hours. The ethereal extract of the cooled solution was washed with sodium carbonate solution, and then shaken with excess of sodium hydrogen sulphite solution. The aldehyde, isolated in good yield from this solution in the usual manner by decomposition with sodium hydrogen carbonate, was a fairly mobile oil, boiling at 122°/12 mm., which did not solidify. It readily underwent oxidation on exposure, and its odour also characterised it as an aliphatic aldehyde:

0·1440 gave 0·4325 CO_2 and 0·0878 H_2O. C = 81·91; H = 6·77.

$C_{10}H_{10}O$ requires C = 82·19; H = 6·85 per cent.

The *semicarbazone*, prepared in the usual manner, redissolved in alcohol, and separated from this solvent in radiating clusters of small needles melting at 174°:

0·1120 gave 20·6 c.c. N_2 at 17° and 730 mm. N = 20·96.

$C_{11}H_{13}ON_3$ requires N = 20·69 per cent.

2-Bromomethylhydrindene (IV).

This compound was easily prepared by heating a solution of 2-hydroxymethylhydrindene (35 grams) in glacial acetic acid saturated at 0° with hydrogen bromide (50 c.c.), at 100° for three and a-half hours.

The compound boiled at 132°/11 mm., and solidified at low temperatures to masses of magnificent prisms, melting at 31°. Its odour was characteristic and reminiscent of aniseed:

0·1742 gave 0·3646 CO_2 and 0·0812 H_2O. C = 57·08; H = 5·21.

$C_{10}H_{11}Br$ requires C = 56·87; H = 5·21 per cent.

It was recovered unchanged after being boiled for ten hours with amalgamated zinc and dilute hydrochloric acid.

...action of 2-Bromomethylhydrindene with Ethyl Malonate.

...yl malonate (6·4 grams) and the bromo-compound (8·4 grams) ...cessively added to a solution of sodium (0·9 gram) in alcohol ...c.). At the temperature of the water-bath a separation of ...m bromide soon commenced, and after ten hours the product ...orked up in the usual manner By distillation under ...ished pressure, well-defined fractions of ethyl malonate, ...methylhydrindene, and finally of the desired ester (7·5 grams) ...btained.

...yl 2-hydrindylmethylmalonate (VI) is a colourless liquid, ...boils at 211°/15 mm., and does not solidify even when cooled ...freezing mixture:

...594 gave 0·4092 CO_2 and 0·1074 H_2O. C 70·00; H 7·48.
   $C_{15}H_{20}O_4$ requires C = 70·35; H = 7·59 per cent.

...e corresponding *acid* was prepared by hydrolysis with alcoholic ...ium hydroxide, and separated from its solution in alcohol in ...ers of small, transparent plates, melting at 174°:

...146 gave 0·4285 CO_2 and 0·0965 H_2O. C 66·93; H 6·14.
   $C_{13}H_{14}O_4$ requires C = 66·66; H = 6·00 per cent.

...*barium, calcium, lead, tin,* and *ferric* salts are insoluble in ...ter, whilst its *magnesium, copper,* and *cobalt* salts are soluble ...d water.

...dihydrazide, $C_6H_4{<}^{CH_2}_{CH_2}{>}CH{\cdot}CH_2{\cdot}CH(CO{\cdot}NH{\cdot}NH_2)_2$, crys

...ts from alcoholic solution in silky needles melting at 177°:
...·5 gave 35·6 c.c. N_2 at 23° and 747 mm. N 21·6.
   $C_{13}H_{18}O_2N_4$ requires N = 21·4 per cent.

Hydrindylpropionic acid, $C_6H_4{<}^{CH_2}_{CH_2}{>}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$,

...epared by heating the above acid at 190° until the evolution ...bon dioxide had ceased. It was readily soluble in benzene, ...paringly so in hot light petroleum (b. p. 90 110°), and ...ted from a mixture of these solvents in small plates melting ...°:

...·3 gave 0·4902 CO_2 and 0·1166 H_2O. C 76·05; H 7·37.
...·4 required 14·6 c.c. $N/10$-NaOH. Equivalent 189·7.
...$H_{16}O_2$ requires C = 75·79; H = 7·37 per cent. M.W. 190.
...*barium* and *magnesium* salts are soluble in cold water, whilst ...ium salt is sparingly soluble, and separates from its solution ...water in needles. Its *ferric, copper,* and *cobalt* salts are ...ble in hot water, its *lead* and *tin* salts sparingly so, and its ...*ric* salt turns yellow when boiled with water.

2-Phthaliminomethylhydrindene (VII).

An intimate mixture of 2-bromomethylhydrindene (1.. ...
with potassium phthalimide (9 grams) was heated at 1.0 ...
nine hours in an apparatus provided with a reflux tube ...
mixture solidified on cooling, and required to be finely ...
before adherent oily matter could be removed by repeated ...
tion with hot light petroleum (b. p. 90—110°). Potassium ...
having then been removed by extraction with hot water, the ...
was crystallised from glacial acetic acid. The compound ...
in small, slender prisms, which were usually somewhat dis... ...
and melted at 174°. The yield was 57 per cent. of the ... ...
and was not improved by carrying out the condensat... ...
presence of sodium iodide:

0·1984 gave 9·0 c.c. N_2 at 16° and 752 mm. $N = 5·30$
$$C_{18}H_{15}O_2N \text{ requires } N = 5·05 \text{ per cent.}$$

2-Hydrindylmethylamine, $C_6H_4{<}{CH_2 \atop CH_2}{>}CH \cdot CH_2 \cdot NH_2$
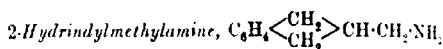
Phthaliminomethylhydrindene (8 grams) was heated ...
centrated hydrochloric acid (35 c.c.) at 180—200° for ... :
and the product was then treated in the usual manner   A ...
proportion of the phthalimino-derivative remained unchar...:
four such experiments furnished a sufficient quantity of ...
boiling at 248°, to permit of its characterisation.

The *hydrochloride* separated from its solution in dilute ...
chloric acid in thin plates with a satiny lustre, melting and ...
posing at 258—260°:

0·1890 gave 12·4 c.c. N_2 at 15° and 751 mm. $N = 7·68$
$$C_{10}H_{13}N, HCl \text{ requires } N = 7·63 \text{ per cent.}$$

The *platinichloride* was obtained as a yellow powder. ...
decomposed at 233°:

0·3614 gave 0·1008 Pt.   Pt = 27·89.
$$(C_{10}H_{13}N)_2, H_2PtCl_6 \text{ requires } Pt = 27·70 \text{ per cent.}$$

The *iodide, sulphate, oxalate,* and *phosphate* are readily ...
in water, whilst the *carbonate* (prismatic needles) and
dichromate (orange, prismatic needles) are soluble in hot wat...

2-Phenylthiocarbamidomethylhydrindene,

$$C_6H_4{<}{CH_2 \atop CH_2}{>}CH \cdot CH_2 \cdot NH \cdot CS \cdot NH \cdot C_6H_5,$$
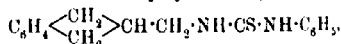
crystallises from alcohol in hexagonal plates melting at 14...

0·1760 gave 15·5 c.c. N_2 at 16° and 745 mm. $N = 10·20$
$$C_{17}H_{18}N_2S \text{ requires } N = 9·93 \text{ per cent.}$$

The Chloride of Hydrindene-2:2-dicarboxylic Acid,

$$C_6H_4{<}^{CH_2}_{CH_2}{>}C(COCl)_2.$$
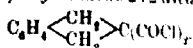
This compound was prepared by the interaction of the calculated amounts of hydrindenedicarboxylic acid and phosphorus pentachloride. It boiled at 173—175°/20 mm., and solidified at the ordinary temperature. It crystallised from light petroleum (b. p. 40°) in clusters of rectangular plates, which melted at 45°, and did not exhibit any marked tendency towards decomposition on contact with the atmosphere:

0.516 gave 0.2952 AgCl.   Cl = 29.02.

$C_{11}H_8O_2Cl_2$ requires Cl = 29.22 per cent

An attempt was made to condense this compound with benzene under the conditions employed by Freund (*Annalen*, 1910, **373**, 1) in the case of diethylmalonyl chloride. It was found that, as in the latter case, the liquor obtained by steam distillation of the product was coloured green, and a small quantity of golden yellow gums was obtained by extraction with ether. There can, therefore, be no doubt that the reaction took the desired course.

Reduction of Ethyl cycloHexanediacetate.

This operation was carried out in the manner already described in the case of ethyl hydrindenedicarboxylate. The oil obtained boiled indefinitely, but small quantities of solid matter separated in the later fractions, boiling at 195—200°/21 mm. This product is sparingly soluble in light petroleum (b. p. 60—80°), and moderately so in benzene. By crystallisation from this solvent crystals, melting at 123°, were obtained:

0.196 gave 0.2848 CO_2 and 0.1046 H_2O.   C = 70.23; H = 10.51.

$C_6H_{13}O_2$ requires C = 70.06; H = 10.06 per cent.

The author hopes to prosecute his investigations in the direction stated as soon as circumstances permit a resumption of the experiments.

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CCLII.—*Studies in the Succinic Acid Series. Part [?]. Anilides and Anilic Acids, and tu[?] [?] Steric Hindrance on the Formation of th[?] [?]*

By George Francis Morrell.

The method of Bouveault and Blanc (*Bull. Soc. ch[?]* [iii], **33**, 879) for the conversion of acids into the corresp[?] alcohols by reduction of their esters in alcoholic solut[?] v[?] sodium frequently gives very unsatisfactory results with th[?] basic acids of the aliphatic series (compare Harries, *Annale[?]* [?] **383**, 167). The original intention of studying the redu[?] other open-chain derivatives of dibasic acids was hinder[?] by [?] lack of suitable methods for preparing them in quantity. Th[?] especially the case with the derivatives of the succinic acid[?] v[?] ring-formation takes place so readily, and the open chain [?] ative forms either a small fraction of the product, or is [?] absent.

The present communication deals with an investig[?] methods and conditions requisite for the production of a [?] yield of certain of the open-chain aniline and ammonia de[?] of succinic acid and its homologues. Whilst with [?] succinic acids the neutral anilides were, under all cond[?] duced only in traces by the action of aniline on the acid[?] anil was generally the sole product, in the case of su[?] the aniline could, by repeated treatment of the succinam[?] as a by-product, be prepared in excellent yield by the [?] under specified conditions. The formation of the five[?] ring is, therefore, apparently facilitated by the presence [?] substituents in the succinic acid. Where the "direct" [?] of preparation failed, good results were obtained by the [?] of aniline on the acid chlorides.

The anilic acids are of importance on account of their [?] the characterisation of the dibasic acid by Auwers' meth[?] the investigation has here been limited to methylsuccinanil[?] as the others have already been fully described by other [?] From an unsymmetrically substituted succinic acid, two [?] anilic acids can theoretically be derived, but although [?] succinanilic acid has been prepared in different ways by [?] investigators, only one of these possible isomerides has [?] isolated. Arppe and Biffi (*Annalen*, 1854, **90**, 111; **91** [?] obtained an anilic acid, melting at 147°, from the anil by [?] the ring with alkali. Anschütz (*Annalen*. 1888, **246** [?]

, likewise prepared the anilic acid both by Arppe's method
and by two methods of his own, namely, the reduction of mesacon-
ic acid, and the action of aniline on methylsuccinic anhydride.
In all cases the acid obtained melted at 143°. Later, Bone and
Sprankling (T., 1899, **75**, 860) give 148—149° as the melting
point and specifically state that they were unable to isolate any
isomeric acid. Auwers (*Annalen*, 1896, **292**, 195) ascribes the
formation of only one anilic acid to the influence of the un-
symmetric molecule, which thus determines the sense in which
the aniline is added to the anhydride, or sodium hydroxide to
the anil. Thus, for example, reaction (1) might proceed to the
entire exclusion of reaction (2):

$$
(1)\ \underset{\mathrm{CH_2 \cdot CO}}{\mathrm{CH_3 \cdot CH - CO}} \Big\rangle \quad \rightarrow \quad \underset{\mathrm{CH_2 \cdot CO \cdot NH \cdot C_6 H_5}}{\mathrm{CH_3 \cdot CH \cdot CO_2 H}}
$$

$$
(2)\ \underset{\mathrm{CH_2 \cdot CO}}{\mathrm{CH_3 \cdot CH - CO}} \Big\rangle \quad \rightarrow \quad \underset{\mathrm{CH_2 \cdot CO_2 H}}{\mathrm{CH_3 \cdot CH \cdot CO \cdot NH \cdot C_6 H_5}}
$$
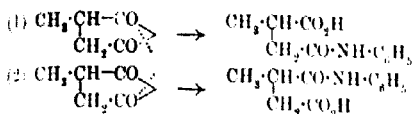
In support of this idea, he states that in the case of methyl
succinic acid, where the lack of symmetry is not so pronounced,
isomeric anilic acids were isolated.

In preparing methylsuccinanilic acid, whether from the anil,
from the anhydride, two points of interest were noted which
seem to indicate the incorrectness of Auwers' and Bone's assump-
tion and the existence of two isomerides in the product. It was
noted that the anilic acid was always precipitated as an oil,
which solidified slowly on keeping, and that never more than
about 40 per cent. of the theoretical yield of the acid, melting
149°, could be isolated. Both of these observations were quite
at variance with those made in the otherwise perfectly analogous
case of succinanilic acid. It seemed scarcely possible that the
existence of an isomeric acid could have been overlooked by so
many investigators, and, indeed, the evaporation of the aqueous
mother liquors to dryness yielded only a very soluble, viscid
residue, which, however, was sufficient in amount to account for
the deficient yield. It was not until it was discovered that both
acids in question were, in aqueous solution, extremely sensitive
to heat, being converted into the above-mentioned viscid products,
that an explanation was forthcoming. So quickly does this trans-
formation occur that the acids cannot even be crystallised un-
altered from hot aqueous solution, as has hitherto been the
case. On attempting to recrystallise a quantity of the pure
substance from water, only 40 per cent. was recovered, and, more-
over, its melting point was 10° lower than when crystallised from
other solvents.

By carefully avoiding anything more than the alightest warm
when dealing with aqueous solutions of the acids, the two struc-
tural isomerides were satisfactorily isolated. They were formed
by taking advantage of their different solubilities in water and
in chloroform. The less soluble methylsuccinanilic acid melts at
159°, and is the main constituent of Anschütz's acid melting at
Its isomeride is much more soluble both in water and in chloro-
form, and melts at 123°. Both acids, on being heated above their
melting points, lose water, and are converted into methylsuccini...

No solution has been arrived at of the problem as to which
the acids the constitution

$$CH_3 \cdot CH(CH_2 \cdot CO_2H) \cdot CO \cdot NH \cdot C_6H_5$$

must be assigned, and to which the alternative

$$CH_3 \cdot CH(CO_2H) \cdot CH_2 \cdot CO \cdot NH \cdot C_6H_5.$$
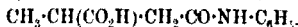
The matter is closely dependent on the constitution of the mes-
aconanilic acid which, on reduction, yields the methylsuccinic
acid melting at 159° (Anschütz, *Ber.*, 1890, **23**, 891). Basing an
argument on an erroneous observation of Reissert (*Ber.*, 1888, **2**
1370) on the oxidation products of mesaconanilic acid, Anschütz
ascribed the constitution (I) to this acid, and, consequently, the
constitution (II) to his methylsuccinanilic acid melting at 143°
(*Annalen*, 1888, **246**, 117):
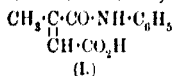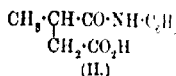
$$CH_3 \cdot C \cdot CO \cdot NH \cdot C_6H_5 \qquad CH_3 \cdot CH \cdot CO \cdot NH \cdot C_6H_5$$
$$\overset{\parallel}{CH} \cdot CO_2H \qquad\qquad CH_2 \cdot CO_2H$$
(I.)   (II.)

Nevertheless, after revising Reissert's work, he convinced him-
self that no light whatever could be thrown on the constitution
of mesaconanilic acid, or of methylsuccinanilic acid, as the result
of oxidation experiments (*Ber.*, 1889, **22**, 747; and *Annalen*, 1889,
254, 137).

It is noteworthy that during the whole of the controversy
these anilic acids between Reissert and Anschütz, the melting point
143°, of methylsuccinanilic acid was not challenged by either of
them. During this present investigation specimens of this sub-
stance, crystallised from water, have been obtained, melting at
143—145°, and having all the appearance of individual substances.
In the first place, many of Anschütz's melting points are some-
what low, as has been pointed out by Auwers, owing to the bad
method of heating which he employed, whereby an incipient de-
composition of the anilic acid sets in at temperatures below the
true melting point. Secondly, these anilic acids should not be
crystallised from water, for although succinanilic acid used seems
to be but little affected, yet others are rapidly attacked. Methyl-
succinanilic acid (m. p. 159°), for example, has never been obtained

ge crystallisation from water with a melting point higher than
l—150°.

The only way open for the preparation of the neutral amides
succinic acid and its homologues is by the action of ammonia
the esters. Other methods lead either to the formation of a
preponderance of the unsymmetrical amide (this vol., p. 1737)
of the imide. The rate of formation of the amides from the
ers and the percentage yield obtained has been found to depend
the ester used and on the extent of substitution in the methylene
are adjacent to the carboxyl, on spatial influence in other
is. The methyl esters react much more quickly than the ethyl
ers, although the yield is about the same in each case. With
substituted methylene groups, that is, with succinic ester itself,
reaction proceeds the most rapidly, and the introduction of
al groups produces a marked decrease, not only in the velocity
ormation, but also in the yield. The reaction has been carried
in a number of different ways for the sake of comparison,
of the methyl and ethyl esters at ordinary and at elevated
peratures, and the most satisfactory results have invariably
obtained by allowing the methyl esters to react at the ordinary
perature with concentrated aqueous ammonia, but instead
owing the liquids to remain in two layers, or using a shaking
time just sufficient alcohol was added to bring the ester into
on In the succinic series this method has given better
than E. Fischer's process, devised for the malonic series,
which the ethyl esters are heated with alcoholic ammonia in
ded tube at 130°, generally for twenty-six hours (*Ber.*, 1902.
44). A comparison of the results obtained in the various
ents, combined with Fischer's results in the malonic series,
teresting :

Acid.	Percentage yield of amide using alcoholic ammonia in bomb.		Percentage yield of amide using aqueous ammonia in cold.	
	Methyl ester.	Ethyl ester.	Methyl ester.	Ethyl ester.
...	—	98		
...malonic	—	40		
...alonic	—	53		
...malonic	—	61		
...ylmalonic	—	2·6		
...lmalonic	—	0·0		
...	63	40	80 (3 days)	80 (12 days)
...uccinic	33		52 (5 ,,)	
...-Dimethylsuccinic .	—		5 (30 ,,)	
Dimethylsuccinic	—		2 (30 ,,)	

yield of amide in the case of succinic acid is therefore com-
le with that obtained with methylmalonic acid, and the sub-

stitution of one only of the four methylene hydrogen atoms in
methyl group produces a marked retardation in velocity ...
diminution in yield. Fischer suggested (*loc. cit.*) that the reaction
with tetramethylsuccinic acid would probably yield only a trace
amide, but it is now evident that this is already the case with ...
dimethylsuccinic acids, the amides of which have now been prepared
for the first time. These results, whilst quite in harmony with
Fischer's hypothesis that the methylene hydrogen is involved in a
reaction in the formation of a preliminary ammonia ...
product, or salt, of the type (III) which decomposes into ...

$$CO_2Et\cdot CMe\vdots C(OEt)\cdot ONH_4 \rightarrow CO_2Et\cdot CHMe\cdot CO\cdot NH_2$$
$$\text{(III.)} \qquad\qquad\qquad \text{(IV.)}$$
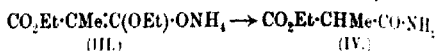
amide (IV), yet show that steric hindrance must be accurate
factor in the case, for there are still in the dimethylsuccinic ...
two methylene hydrogen atoms similar to the one in methylene ...
acid, yet the velocity of the amide-formation and the yield of am
are enormously greater in the latter case, whereas if the presence
of an unsubstituted methylene hydrogen atom were the sole ...
tioning factor we should expect the acids to behave similarly, ...
least that more than mere traces of dimethylsuccinamide would be
produced. Moreover, the results with the constitutionally different
cis- and *trans*-dimethylsuccinic acids are different, the *cis* react
more slowly than the *trans*-acid, as one would expect from con-
siderations of spatial interference.   The conclusion is there-
drawn that the accumulation of substituent groups round
esterified carboxyl group hinders the reaction with ammonia ...
although some methylene hydrogen is still unsubstituted.

EXPERIMENTAL.

Succinanilide.

Succinanilide was obtained by Menschutkin (*Annalen, *
162, 187) in 25 per cent. yield by the direct action of aniline
succinic acid. It can be obtained in better yield by the action
of succinyl chloride on a solution of aniline in benzene (see also
this vol., p. 1736, and Dunlop and Cummer, *J. Amer. Chem.*
1903, **25,** 612). Since this method involves the previous prepara-
tion of succinyl chloride, which is itself obtained at most in 75
cent. yield, the following direct method of preparation from the
acid is preferred.

Twenty grams of succinic acid were heated for three to four hour
at 200° (thermometer in the liquid) with 40 grams of aniline ...
very short reflux air-condenser was used, so that only the aniline
was condensed, the water generated by the reaction being all

escape, as it was found that if condensed and returned to the ... the temperature of the boiling mixture eventually sank as ... at 125°, and the unsatisfactory yield described by Menschutkin ... obtained. The product was poured into dilute acid, and when ... the precipitate of anilide and anil was collected and warmed ... an excess of dilute aqueous sodium hydroxide, whereby the ... was dissolved as sodium succinanilate, but the anilide was ... attacked. The latter was collected, and after one crystallisation ... alcohol was quite pure. From the aqueous solution of the ... succinanilate dilute hydrochloric acid precipitated succinanilic acid ... in almost pure condition. The above amount of succinic acid ... 10 grams of anilide and 25 grams of anilic acid, an almost ... theoretical yield.

Succinanilide crystallises from alcohol in short, stout needles, ... melting at 230° (Menschutkin gives 227°). It is quite insoluble in ... water, and is not acted on by boiling dilute alkali hydroxide. It is ... soluble in about 35 parts of boiling alcohol, and 460 parts at 16°, ... and almost insoluble in the other common organic solvents.

Conversion of Succinanilic Acid into Succinanilide.

The anilic acid obtained as a by-product in the above preparation ... is readily converted into the anilide by heating with 75 per ... cent. of its weight of aniline in sealed tubes at 110—115° for forty ... eight hours. The product is a mixture of anilide and anil with ... some of aniline, similar to that obtained in the direct preparation, ... the anilide is separated by treatment with hydrochloric acid ... then with sodium hydroxide exactly as there described. From ... grams of anilic acid 12 grams of anilide were obtained, and ... grams of anilic acid recovered (compare Tingle and Cram, *Amer. ... J.*, 1907, **37**, 597, who obtained only a 25 per cent. yield ... five days' heating in an open vessel). By repeating this ... process with the recovered anilic acid it is eventually almost ... entirely transformed, giving a total yield of about 30 grams of ... succinanilide from the 20 grams of succinic acid originally taken.

Methylsuccinanilide.

This has been briefly described in a previous paper (this vol., ... 1736). Unlike succinanilide, it could be obtained only in traces ... the action of aniline on either the free methylsuccinic acid or ... anilic acid. Under all experimental conditions tried, ring ... ation ensued with the almost exclusive production of the anil. ... contrast with succinanilide it is very readily soluble in alcohol, ... fairly soluble in ethyl acetate, sparingly so in chloroform, and ... soluble in water or benzene.

Methylsuccinanil.

This was obtained in almost theoretical yield by an improved of Kling's process (*Ber.*, 1897, **30**, 3040). Ten grams of succinic acid were gently boiled for a few minutes with of aniline in an inverted retort. The retort was then reversed the mixture distilled as rapidly as possible. No carbonisation occurred, and the distillate solidified to a of the anil, which after one crystallisation from much formed clusters of tiny needles melting at 109—11 gives 104°, and Kling 107°).

Methylsuccinanil is very readily soluble in alcohol, chloroform, or benzene. It is soluble in about 40 parts water, and to the extent of 0·28 per cent. in water at 1

Methylsuccinanilic Acids.

An aqueous solution of the sodium salts of the two isomers was prepared either by dissolving the product of the aniline on methylsuccinic anhydride in cold sodium solution, or methylsuccinanil in aqueous sodium hydroxide aid of gentle heat. The isolation of the two isomerides was plished by fractional precipitation of the acids from combined with fractional crystallisation from chloroform. experiment 7·7 grams of methylsuccinanil were dissolved of 2N-sodium hydroxide, and to the filtered solution hydro acid was slowly added with constant agitation. No oil was tated, but a clear solution was obtained, from which moments crystals of the anilic acid separated. The fractions were obtained: (1) After the addition of 2N-hydrochloric acid 1·9 grams were deposited, melting which, when recrystallised twice from ethyl acetate, me 158—159°. (2) On adding a further 10 c.c. of 2N-hydr acid, 2·8 grams were deposited, melting at 95—135°, when extracted with cold chloroform. The residue (1·3 grams) of the acid melting at 159°, and after crystallisation from acetate melted at this temperature. The solution contained the isomeric acid, and it was added to the chloroform solution below). (3) On keeping overnight, 1·0 gram of material melting at 85—95°. This was the fairly pure isomeric acid, almost entirely soluble in cold chloroform.

The united chloroform solutions were precipitated with petroleum, and the precipitate (m. p. 105—108°) was a process of alternate precipitation from the aqueous solution sodium salt, and recrystallisation from chloroform. This

successful because the difference in the solubility of the iso-
meres in water was not so great as in chloroform. Eventually a
product was obtained melting at 123°, which consisted of broad,
minute, microscopic needles, and further treatment produced no
alteration in the melting point.

The less soluble acid appeared to form from 40 to 45 per cent.
the total product, but, of course, the more soluble acid could
not be isolated in a pure condition in quantity anywhere
approaching the amount (55—60 per cent.) in which it was
present.

In order to remove all doubt as to the chemical individuality
these two acids, the following data were obtained.

Methylsuccinanilic acid, m. p. 159°, crystallises from ethyl
acetate in fairly broad, flat needles. It is very readily soluble in
alcohol, moderately so in ethyl acetate, and very sparingly so in
chloroform (about 0·05 per cent. at 18°) or water (0·09 per cent.
at 15°. When heated above its melting point it is converted into
anil, melting at 109°:

0·2041 gave 0·2361 CO_2 and 0·0597 H_2O. C = 63·69; H = 6·56.
0·1566 ,, 9·2 c.c. N_2 at 15° and 749 mm. N = 6·85.
$C_{11}H_{13}O_3N$ requires C = 63·76; H = 6·28; N = 6·76 per cent.

Methylsuccinanilic acid, m. p. 123°, crystallises from chloroform
in clear, broad, microscopic needles. It is extremely readily soluble
in alcohol or ethyl acetate, very readily so in hot chloroform, and
chloroform solution contains 1·6 per cent. at 16°. It is fairly
easily soluble in hot benzene, insoluble in light petroleum, and
moderately soluble in water (1·2 per cent. at 15°). When heated
to its melting point it is converted into the anil melting at 109°;
a mixture with the anilic acid melting at 159° melted at 105—108°,
and when this mixture was recrystallised fern-like clusters of the
anil mixture type were obtained:

0·2037 gave 0·2225 CO_2 and 0·0554 H_2O. C = 63·43; H = 6·43.
0·1294 ,, 7·1 c.c. N_2 at 16° and 760 mm. N = 6·94.
$C_{11}H_{13}O_3N$ requires C = 63·76; H = 6·28; N = 6·76 per cent.

Succinamide.

This compound can be obtained only in minute quantity by the
action of ammonia on succinyl chloride. It was prepared, however,
a variety of ways indicated in the introductory portion, and in
per cent. yield by the action of concentrated aqueous ammonia
methyl succinate, just sufficient alcohol being added to the
mixture to bring the ester into solution. After three days the
action was complete, and the precipitated amide was found to be

almost pure without further treatment. It crystallises from water in short, stout needles, melting and decomposing at 195°. This is considerably higher than the melting point usually given, and if the temperature rises slowly a much lower value is usually obtained. One part of the amide dissolves in 15 parts of boiling water, and in 300 parts of water at 15°. It is almost insoluble in alcohol and other organic solvents.

Methylsuccinamide.

This was prepared most readily in the same way as succinamide, by the action of concentrated aqueous ammonia on a solution of the methyl ester of the acid. After remaining for five days at the ordinary temperature no more amide was deposited, and the total yield then amounted to 52 per cent. of the theoretical. Methyl-succinamide crystallises from water in short needles, melting and decomposing at 225°. It is almost insoluble in alcohol and other solvents, but soluble in about 50 parts of water at 15°, and very soluble in hot water.

cis- and trans-Dimethylsuccinamide.

[With SIDNEY HENRY GROENEWOUD.]

The only mention of a dimethylsuccinamide in the literature is by E. von Meyer (*J. pr. Chem.*, 1882, [ii], **26**, 359), who states that he prepared it by the action of ammonia on the oily product obtained by the bromination of cyanethine. The salt is described as crystallising in fine, pyramidal, pointed prisms, and did not melt at 260°. That it could really have possessed the constitution assigned to it by von Meyer seems impossible as these properties agree in no way with those of either the *cis*- or *trans*-amide obtained by a method which admits of no doubt, namely, from the respective esters by the action of ammonia. It seems, moreover, improbable that the symmetrical amides could be obtained in any appreciable quantity by the action of ammonia on the acid bromides, even if such were present in the oil obtained from cyanethine.

cis-Dimethylsuccinamide was obtained by the action of concentrated aqueous ammonia on dimethyl *cis*-dimethylsuccinate (m. p. 200°), prepared according to Zelinski's method (*Ber.*, 1891, **24**, 646), sufficient alcohol being added to make the alcoholic strength of the resulting solution about 33 per cent. After being kept for one month at the ordinary temperature 0·06 gram of amide separated in well-formed, triclinic prisms from a solution containing 3 grams of the ester. The mother liquors yielded on evaporation

and consisting apparently in the main of unchanged ester, but treating this a second time with ammonia no less than 0·6 gram crystals separated in fourteen days. The crystals obtained by is operations, after washing with alcohol, were quite pure without other treatment. They melted and decomposed at 244°, and were most insoluble in alcohol or cold water, but fairly readily soluble in water:

·951 gave 16 c.c. N_2 at 22° and 767 mm. N = 19·49.

$C_6H_{12}O_2N_2$ requires N = 19·44 per cent.

trans-*Dimethylsuccinamide* was obtained in a precisely analogous manner to the *cis*-amide by substituting the *trans*- for the *cis*-methyl ester in the experiment described above. Under similar conditions 3 grams of the *trans*-ester yielded a larger amount of amide in the first treatment, namely, 0·15 gram. It was deposited in monoclinic prisms of similar appearance, and solubilities in alcohol and water, as the *cis*-isomeride. It melted and decomposed at 238°:

·198 gave 18·6 c.c. N_2 at 20° and 760 mm. N = 19·63.

$C_6H_{12}O_2N_2$ requires N = 19·44 per cent.

Both amides were decomposed extremely slowly by boiling hydrochloric acid, more rapidly by boiling potassium hydroxide solution. Unfortunately the quantities at our disposal were too small for the purification products to be satisfactorily identified, but since the been regenerated their corresponding acids on hydrolysis and it remotely improbable that the action of cold ammonia would induce any change of configuration, it may be confidently assumed at the amides, also, yield on hydrolysis the respective acids from which they were obtained.

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    London, E.C.

LIII.—*A Magnetic Study of Compounds of Water and of Aqueous Solutions.*

By Francis William Gray and William Milne Birse.

The object of the work described in the present paper was to ascertain whether magnetic measurements can throw any light on the state of combination of water in compounds of different types, and especially to measure the magnetic properties of water in (1) aqueous salt solutions, (2) hydrated crystals such as those of zinc sulphate, and (3) organic acids, such as benzoic and oxalic acids, which may be regarded as compounds of their anhydrides with water.

In all these classes instances were found in which the additivity, in the molecular sense, is obeyed. Thus aqueous solutions of potassium ferricyanide obey the law of additivity throughout the whole range of concentration, and yield a more trustworthy value for the susceptibility of potassium ferricyanide than is obtained from the solid.

In the case of copper sulphate, if it is assumed that the susceptibility of the water is not affected appreciably by the salt in it, it is found that the paramagnetic susceptibility of the anhydrous copper sulphate molecule is increased by about 11·5 per cent. when it unites with one molecule of water. Further addition of water molecules to form the higher hydrate has no marked influence on the susceptibility.*

In the case of organic acids it is found that additivity, in a molecular sense, holds for benzoic, phthalic, maleic, and fumaric acids, but not for succinic and camphoric acids.

Aqueous solutions of potassium ferricyanide obey the law very nearly the equation $\frac{x}{10·07} - \frac{y}{0·72} = 1$, where x = the weight of potassium ferricyanide in 100 grams of aqueous solution, and $y \times 10^{-6}$ denotes the susceptibility of a solution of percentage x. It is not usual for an aqueous solution to follow so closely the additive law. Indeed, many of the older determinations of the susceptibility of salts are quite valueless, since they were deduced from determinations of solutions of single concentrations on the basis of additivity, and the value obtained in this way varied usually according to the concentration of the solution. Cuvier and Moles (Arch. Sci. phys. nat., 1913, [iv], 35, 425) have shown how the atomic susceptibility of iron varies with the concentration in solutions of ferric chloride, ferric nitrate, and sodium pyrophosphate.

In the magnetic study of solutions the following effects are to be looked for: (1) ionisation, (2) union of two or more molecular magnets to yield an astatic system not oriented in a magnetic field, (3) formation of hydrates and the stability of the same, (4) hydrolysis. In addition, care must be taken to ascertain whether or not the susceptibility of a solution changes with time. Instances have been found of solutions originally additive which showed a gradual departure from additivity. Heydweiller (Ber. Deut. physikal. Ges., 1913, 15, 112) gives results for solutions of ferric chloride, manganese sulphate, and nitrate, nickel nitrate, chromic sulphate, chromic nitrate, and cobalt nitrate. He observed a maximum in the curves for the relation between concentration and molecular

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* It is well known that similar differences have been observed in the spectra and heats of hydration for the different water molecules in polyhydrates.

...ibility. This maximum may be produced by the joint action ...ect (1), which causes increase of susceptibility, and effect (2), ...h causes diminution of susceptibility. Oxley discusses effect (3) ...*Camb. Phil. Soc.*, 1912, **16**, 421), and points out that the ...ate may be so unstable as not to affect the magnetic properties ...g Wiedemann claims from magnetic measurements to be able ...culate the degree of hydrolysis of ferric chloride in aqueous ...ions. In aqueous solutions of potassium ferricyanide which ... to obey the additive law none of the above effects can be ...ted by the present method.

...ang $\frac{x}{1007} - \frac{y}{0.73} = 1$ and putting $x = 100$, we obtain for the sus-

...bility of potassium ferricyanide the value $+6.43 \times 10^{-6}$. This ... 10.97, or very nearly 11 magnetons per molecule. Weiss ...*pt. rend.*, 1911, **152**, 367) gives 10.41 magnetons.

...he susceptibility of solid potassium ferricyanide (powder) wa ...d to be $+6.77 \times 10^{-6}$, the error-range being ± 0.16, or about ... per cent. (when calculated by the average deviation method). ...figure, 6.77, gives 11.26 magnetons per molecule.

...le (*Ann. Physik*, 1913, [iv], **41**, 829) points out, in the case ...aramagnetic powders, that the molecules at the surface of the ...s are most easily oriented in the magnetic field. An increase ...e size of the particles causes a diminution in the total surface, ...therefore in the number of surface molecules, and thus a fall ...e susceptibility. This was found to hold for powdered potass ...ferricyanide.

...n the other hand, the increased density which accompanies ...ased size of particles tends to an increased value for the ...eptibility.

...n the whole, therefore, with potassium ferricyanide, the sus ...ability obtained from solutions is more trustworthy than that ... powders, because with solutions the precision is much better, ...law of additivity is obeyed throughout the whole range of ...entrations, and, further, the result implies an integral number ...magnetons per molecule.

...n order to account for the magnetic difference between copper ...ate monohydrate and copper sulphate pentahydrate, we ...est the following hypothesis: that the water-molecules are ...ged in space round the outside of the copper sulphate molecule, ...in the vicinity of each oxygen atom and one in the vicinity ...he copper atom. The last-mentioned water-molecule is the only ...that causes deviation from the additivity of the magnetic ...perties. When two copper atoms of two anhydrous copper ...hate molecules are near one another they hamper one another's ...ment in the magnetic field. Thus the orientation of the copper

atom is not so free in the anhydride as in the monohydrate
the pentahydrate, in both of which water-molecules intervene
between the copper atoms, keeping them apart and thus prevent
the mutual action above referred to.   In other words, the
magnetic susceptibility of the copper atom is less in the anhydride
than in the monohydrate or in the pentahydrate.

This theory receives support from the fact that similar hypotheses
have served to explain two observations recently made in the cryo-
genic laboratory at Leiden.   Perrier and Onnes (*Compt. rend.*,
1914, **158**, 941) studied mixtures of liquid oxygen and liquid
nitrogen, and found that the coefficient of magnetic susceptibility
of liquid oxygen increases as the concentration diminishes. Again,
Onnes and Oosterhuis (*Proc. K. Akad. Wetensch., Amsterdam*,
1913, **15**, 969) in studying paramagnetism at low temperatures
found for hydrates of salts and anhydrous salts, in the case of
ferrous sulphate and manganese sulphate, that whilst the hydrates
obeyed Curie's law, $\chi T = $ constant, down to the temperature of
liquid nitrogen, the anhydrous salt followed the law, $\chi(T + \Delta) = $
constant, where $\chi = $ specific susceptibility, $T = $ absolute temperature,
and $\Delta = $ a constant.   Thus, at any given temperature within a
certain range the paramagnetism is increased by the union of
water with the salt.

Mlle. Feytis (*Compt. rend.*, 1911, **153**, 668) about the same time
as we made our observations obtained similar results for copper
sulphate (see experimental part).

Mlle. Feytis (*loc. cit.* and *Compt. rend.*, 1913, **156**, ...)
for the salts $CuCl_2,2H_2O$, $CuCl_2,2NH_4Cl,2H_2O$, $CuCl_2,2KCl,2H_2O$,
and $NiSO_4,6H_2O$ departure from additivity in the same sense as
copper sulphate.   On the other hand, she observed that additivity
held for the salts $CoSO_4,7H_2O$, $Cr_2(SO_4)_3,16\cdot74H_2O$, and

$$K_2SO_4,Cr_2(SO_4)_3,24H_2O,$$
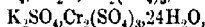
but not for $CrCl_3,6H_2O$, for which the departure was in a direction
opposite to that for copper sulphate.   This last case may be brought
into line with our hypothesis by supposing that in anhydrous
chromic chloride the chlorine atoms are arranged symmetrically
round the chromium atom, chlorine atoms keeping apart the
chromium atoms of different salt molecules, and thus enhancing the
paramagnetism.   When water unites with the anhydrous salt
we suppose that there is no longer the symmetry referred to, so
that chromium atoms can come nearer one another than before,
and thus the atomic paramagnetism of the chromium is diminished.
The hydrates of chromic chloride are represented thus:
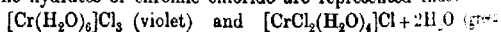
$[Cr(H_2O)_6]Cl_3$ (violet)   and $[CrCl_2(H_2O)_4]Cl + 2H_2O$ (green).
The difference between these is not shown in magnetic measure-
ments.

We have observed departure from additivity in the hydrates of magnetic salts also, and from our own results and those of others are been led to the general rule, that when there is departure from additivity a **paramagnetic** anhydride has its paramagnetism raised and a **diamagnetic** anhydride has its diamagnetism raised by the union with water, on the assumption that the susceptibility of the water is not affected appreciably by the union. In a paramagnetic substance the always present diamagnetism is hidden by the larger paramagnetism. According to our general rule, the diamagnetism in a paramagnetic substance might be increased by union with water (when there is departure from additivity), and thus the apparent paramagnetism would be reduced. We believe, however, that the departure from additivity in paramagnetic salts can be only partly explained by this cause, and that the hypothesis suggested under copper sulphate, or a substitute, is still required.

For copper sulphate pentahydrate the theory might be brought forward that the water of crystallisation is made up of two dihydrol molecules and one monohydrol molecule, or one trihydrol molecule and two monohydrol molecules, or one trihydrol molecule and one hydrol molecule, or one dihydrol molecule and three monohydrol molecules, or five monohydrol molecules. The first of these five possibilities is best suited for explaining how one water-molecule differs from the other four. We think, however, that this would account for only a very small magnetic difference, judging from the results of Piccard (*Compt. rend.*, 1912, **155**, 1497), who studied the susceptibility of water at various temperatures from 0° to 100°. The susceptibility of water is only 0·75 per cent. greater at 100° than at 0°; also the decrease on solidification is 2·4 per cent., so that variations in the proportions of trihydrol, dihydrol, and mono- has very little effect on the susceptibility.

Similarly the results of Piccard do not encourage us to suppose a departure from additivity in a hydrate is due to any appreciable extent to any change in the magnetic susceptibility of the water, that is, to change caused by the union with the anhydride.

The water which is present in a paramagnetic metallic hydroxide usually regarded as a clear case of water of constitution, and as water unites with the oxide to form the hydroxide there is a considerable enhancing of the paramagnetic susceptibility of the oxide molecule. Thus, there are hydrates and hydroxides in which the magnetic rôle of water is identical, and it becomes an interesting question whether we can extend the hypothesis we have for hydrates to the case of metallic hydroxides.

With regard to the organic acids (see tables III and IV) the relation between constitutional and magnetic similarities and

differences is interesting. In every case except the two acids which show decided departure from additivity (succinic and camphoric acids), the anhydride is obtained from the interaction of the carboxyl groups which are either near one another in the same molecule or are in different molecules, so that interaction can take place without any great change in the configuration of the atoms and their electrons. On the other hand, with succinic acid there is a marked change in the relative position of the atoms when the two carboxyl groups at the ends of the open chain interact to form a cyclic compound, and similarly with camphoric acid when two carboxyl groups attached to two non-adjacent carbon atoms in the camphoceanic ring interact to give the anhydride.

In comparing our results with Pascal's it should be noted that we use for the molecular susceptibility of water the experimental value $-12\cdot96 \times 10^{-6}$, whilst the sum of Pascal's atomic values $-10\cdot46 \times 10^{-6}$. In calculating the molecular susceptibility of organic compound, however, Pascal introduces corrections for substitution, so that the two methods are not necessarily the same. At any rate, our experimental figures and Pascal's calculated values agree for fumaric acid and maleic acid and benzene; also according to our method, additivity holds for these three substances.

EXPERIMENTAL.

The recent concordant results of de Haas and Draper (?), of Weiss and Piccard (1913), and of Sève (1912) yield for the specific susceptibility of water reduced to a vacuum the value $-0\cdot72 \times 10^{-6}$, which we use here in preference to the value $-0\cdot75 \times 10^{-6}$ formerly used by Pascal, and the still different one of Curie, namely, $-0\cdot79 \times 10^{-6}$.

All our results were obtained with a Curie-Chéneveau torsion balance except number 8 of table III, for which a Pascal balance was used. The permanent magnet of the Curie-Chéneveau balance had an average field of 232 gauss per sq. cm. over an area 5·6 sq. cm. round and at right angles to the axis. Four torsion wires were used about 33 cm. long and of diameter ? mm., 0·10 mm., or 0·07 mm., according to the requirements. The scale was placed at a distance of more than 2 metres from the mirror. The greatest precision was obtained with a pure liquid, for example, with benzene, as shown in table III. All the weights in table III were in the form of powder, and the precision was usually not so great as with benzene. In some cases we increased the precision by heating the anhydride both before and after it in the tube, or by leaving the filled tube in a vacuum desiccator for some time before the determination. With a glass tube the heat might cause volume changes resulting in error, and it occurred

... try a quartz tube.[*] We found, however, that little, if any ... was gained by its use, as the susceptibility of the quartz was ... greater than that of the glass we used, so that a degree of ... certainty was introduced which perhaps more than balanced ... advantage obtained from the constancy of volume of the quartz. In the case of the substances in table IV we sometimes found ... purification improved the precision, even when the method of ... fication produced no change in the melting point.

Result number 8 in table III was obtained with a Pascal balance, ... field of the electromagnet having an average of about 9000 ... per sq. cm. over an area of 2·21 sq. cm. at right angles to ... round the axis.

The determinations were carried out at 15°.

In the following numerical results we have given as many digits ... obtained in our calculation. The precision of the estimation ... cates how many digits should be retained in each case.

Magnetic Susceptibility of Aqueous Solutions of Potassium Ferricyanide.

TABLE I.

Reference letter or number.	Number of measurements.	x.	y.	y_1.	d_1.	y_2.	d_2
A	3	29·13	+1·394	+1·362	+0·032	+1·354	+0·040
B	2	26·22	+1·188	+1·155	+0·033	+1·148	+0·040
C	3	23·53	+0·993	+0·962	+0·031	+0·956	+0·037
	2	20·35	+0·731	+0·735	−0·004	+0·731	0·000
	2	17·32	+0·513	+0·518	−0·005	+0·515	−0·002
	2	15·55	+0·391	+0·392	−0·001	+0·390	+0·001
	3	12·37	+0·162	+0·164	−0·002	+0·163	+0·001
	1	11·08	+0·0675	+0·0722	−0·0047	+0·0718	0·0043
	2	8·27	−0·123	−0·129	+0·006	−0·128	+0·005
	1	7·416	−0·178	−0·189	+0·011	−0·188	+0·010
	4	6·005	−0·286	−0·291	+0·005	−0·289	+0·003
	4	4·594	−0·383	−0·392	+0·009	−0·390	+0·007
	6	2·976	−0·506	−0·507	+0·001	−0·504	0·002

In table I, x denotes the weight of potassium ferricyanide in ... grams of aqueous solution, $y \times 10^{-6}$ denotes the susceptibility ... by experiment for a solution of percentage x. y_1 is the ... of y as obtained from $\dfrac{x}{10\cdot07} - \dfrac{y}{0\cdot72} = 1$. d_1 denotes the distance ... the direction of y that the experimental point is above or below ... straight line; + means above, − means below. Under y_2 and ... are given corresponding values obtained from $\dfrac{x}{10\cdot07} - \dfrac{y}{0\cdot716} = 1$.

... jecting the three solutions A, B, and C, we note that the first ... ight line fits the experimental points very closely, and that the ... nd line fits still closer, but does not pass through the water... ... However, taking into account the degree of uncertainty of

the measurements and seeing how near the lines lie to one another
we need not push the refinement of the calculation so far, and shall
be content with the first and simpler equation.

Of the solutions, A was the most concentrated we could conveniently use, and its composition was found by chemical means.
By adding a weighed amount of A to a weighed amount of water,
B and C were obtained. S was prepared by adding a weighed
amount of water to a weighed amount of pure potassium
cyanide. A stock of S was prepared, from which, by the weighing
method, the series of solutions 1 . . . . 9 were obtained. Thus
any error in the determination of the composition of A will affect
B and C, and any error in the preparation of S will affect the series
1 to . . . . 9. The two sets are, of course, independent of one another.
This explains why the three points obtained with A, B and C
deviate further from the straight line than any of the points in the
set S, 1, ... 9. It is probable that the analysis of A by
chemical means is not so accurate as the preparation of S by the
weighing method.

The degree of the uncertainty of the magnetic measurements
of the solutions will be seen from solution 9, for which the mean
deviation from the mean was 0·0038 or 0·76 per cent.

<div style="text-align:center">TABLE II.</div>

Substance.	Specific susceptibility × 10⁶.		Average deviation from mean.		Molecular susceptibility × 10⁶.	
	Mlle. Feytis' values.	Our values.	Absolute.	Per cent.		
$CuSO_4$	8·6	8·39	0·02	0·2	1339	
$CuSO_4.H_2O$	8·6	8·32	0·04	0·5	1479	
$CuSO_4.5H_2O$	5·9	5·81	0·03	0·5	1450	

Molecular susceptibility of $CuSO_4.H_2O$	1479
Correction for water	−13
Susceptibility of the molecule $CuSO_4$ in $CuSO_4.H_2O$	1492
Molecular susceptibility of anhydrous $CuSO_4$	1339
Difference	153

Thus, the union with one molecule of water has increased the
paramagnetic susceptibility of the anhydrous copper sulphate molecule by $+153 \times 10^{-6}$ or by about 11·5 per cent. Further addition
of water molecules to form the higher hydrate has no marked influence on the susceptibility.

Otherwise :

Substance.	Molecular susceptibility × 10⁶.		Deviation from additivity
	Experimental.	Calculated.	Absolute. Per cent.
$CuSO_4.H_2O$ ...	1479	+1326 (from $CuSO_4$ and H_2O)	153
$CuSO_4.5H_2O$ ...	1450	+1427 (from $CuSO_4.H_2O$ and H_2O)	23

Copper Nitroprusside.

	Specific suscep- tibility ×10⁶.	Average deviation from mean		Number of measure- ments.	Molecular suscep- tibility ×10⁶	Deviation from additivity per cent.
		Abso- lute.	Per cent.			
CuₓFe(CN)₅,2H₂O	+4·54	0·05	1·0	5	+1432	8·4
CuₓFe(CN)₅	+5·73	0·03	0·5	5	+1593	—

This would indicate that the deviation is opposite in direction to that for copper sulphate. However, any slight decomposition in the preparation would make the anhydride too highly paramagnetic. A general study of nitroprussides, on which we are at present engaged, may throw more light on this question.

Some Diamagnetic Salts.

Potassium ferrocyanide:

$$\text{Molecular susceptibility of } K_4Fe(CN)_6,3H_2O = -172\cdot0\times10^{-6}$$
$$\text{Correction for } 3H_2O = -38\cdot9$$
$$\text{Susceptibility of the molecule } K_4Fe(CN)_6 \text{ in } K_4Fe(CN)_6,3H_2O = -133\cdot1$$
$$\text{Molecular susceptibility of anhydrous } K_4Fe(CN)_6 = -145\cdot1$$
$$\text{Difference } 12.$$

On union with water the diamagnetism of the molecule Fe(CN)₆ is diminished by about 9 per cent.

The following figures were calculated from the results of St. Meyer. Loss per cent. means the percentage by which the diamagnetic susceptibility of the anhydrous salt molecule is reduced by union with water to form the given hydrate.

Hydrate	MgCl₂,6H₂O.	CaCl₂,6H₂O	BaCl₂,2H₂O.
Loss per cent	over 100	over 100	25
Hydrate	MgSO₄,7H₂O.	Li₂SO₄,H₂O.	Na₂CO₃,10H₂O.
Loss per cent.............	over 100	24	over 100

This would imply that in these salts we have paramagnetism added by the diamagnetism of the water.

TABLE III.

Organic Acids.

Reference number. Substance.	Specific susceptibility ×10⁶	Average deviation from mean		Number of measure- ments.
		Absolute.	Per cent.	
1. Benzene]	−0·7086	0·0049	0·7	5
2. Benzoic acid ...	−0·5560	0·0123	2·2	6
3. Benzoic anhydride ...	−0·5522	0·0060	1·1	6
4. Phthalic acid ...	−0·4878	0·0054	1·1	7
5. Phthalic anhydride ...	−0·4460	0·0048	1·1	6
6. Maleic acid	−0·4269	0·0182	4·0	8
7. Fumaric acid ...	−0·4158	0·0043	1·0	4
8. Fumaric acid ...	−0·4269	0·0095	2·2	5
9. Maleic anhydride ...	−0·3654	0·0056	1·5	6

TABLE III. (continued).

Reference number. Substance	Specific susceptibility × 10⁶.	Average deviation from mean.		λ
		Absolute.	Per cent.	d
10. Succinic acid ...	0·4615	0·0015	0·3	
11. Succinic anhydride ...	— 0·4753	0·0111	2·3	1
12. Camphoric acid	0·7461	0·0054	0·8	
13. Camphoric anhydride ...	— 0·6294	0·0172	2·7	1

TABLE IV.

Reference number. Substance.	Molecular susceptibility × 10⁶.		Deviation from additivity. Per cent.	
	Experimental.	For additivity.		
2. Benzoic acid...	67·78	68·85	1·5	
3. Benzoic anhydride ...	62·37 × 2	—		
4. Phthalic acid...	81·36	78·97	2·5	
5. Phthalic anhydride ...	— 66·01	—		
6. Maleic acid ...	49·52	— 48·77	1·5	
7. Fumaric acid...	48·23	— 48·77	1·0	
8. Fumaric acid ..	49·52	— 48·77	1·5	
9. Maleic anhydride ...	35·81	—		
10. Succinic acid...	54·45	60·49	9·9	
11. Succinic anhydride ...	47·53	—		
12. Camphoric acid	149·3	— 125·3	19·0	
13. Camphoric anhydride ...	112·3	—		

	Molecular susceptibility × 10⁶	Pascal gives	
Benzene.........................	— 55·27	— 55·1 (Expt.)	
Phthalic acid	— 81·36		
Mean	— 68·31		
Benzoic acid	— 67·78		

Thus when the molecular susceptibility of benzoic acid is calculated from benzene and phthalic acid on the basis of additivity then the experimental result differs from this calculated value less than 1 per cent.

Under the heading " Pascal " we give the molecular susceptibilities as calculated from Pascal's atomic values and his correction for constitution.

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Organic Chemistry.

Isoprene from Commercial Turpentines. Chas. H. Herty and D. Graham (*J. Ind. Eng. Chem.*, 1914, **6**, 803—804).—Ordinary oil of turpentine yielded 5·5% of isoprene when submitted to distillation in an "isoprene lamp" apparatus described by Harries and Gottlob (*A.*, 1911, i. 798); the fraction of oil of turpentine, b. p. 155—156°, had 80% of isoprene, and the fraction b. p. 160—175°, 0·5%. No isoprene was obtained from the fraction b. p. above 175°. It is evident that the isoprene is derived from the pinene present. Oil of *Pinus* pinea yielded 12% of isoprene; pine oil, 4%; and refined spruce pine pine, none.
W. P. S.

Ethyl Ester of Linolic Acid Tetrabromide as a Product in the Analysis of Cotton-seed Oil. Leroy S. Palmer and Philip Wright (*J. Ind. Eng. Chem.*, 1914, **6**, 822—823).—During an investigation regarding the composition of cotton-seed oil, in which the saturated fatty acids were isolated by making use of their solubility in ether, the authors obtained a crystalline compound, in place of linolic acid tetrabromide, when an attempt was made to form the latter substance. The crystals had m. p. 58—58·5°, and consisted of ethyl linolate tetrabromide. The cause of the formation of this ethyl ester has not been definitely ascertained, but it appears to take place during the time the lead soaps are in contact with ether.
W. P. S.

Humic Acid. Sven Odén (*Arkiv. Kem. Min. Geol.*, 1914, **5**, 25. Compare A., 1912, i, 336; this vol., i, 500).—When suspensions of *Sphagnum*, *Sphagnum* peat and leaf humus are treated with ammonia, absorption of **ammonia** takes place, and, coincidently, salts are set in considerable amounts from the peat and humus, whilst the humus itself gives only a relatively insignificant amount of salt. These results are opposed to the view of Baumann and Gully, who infer that the adsorption of bases by peat is mainly due to the presence of *Sphagnum* cells. The effect on conductivity of the action of salts exceeds that of adsorption even in concentrations *N* 001. Humates are extracted by ammonia in concentrations as *N* 00005, so that the suggestion that humates are decomposition acids of the action of ammonia on humus is improbable.

With reference to the criticisms of Ehrenberg and Bahr (this vol., it is pointed out that filtration through collodion can only be relied on when not less than 10% collodion is employed. It is also quite possible that as Ehrenberg and Bahr omitted to extract humic acid with alcohol, it may have contained a considerable amount of hymatomelanic acid which might account for the different obtained for the mol. weight.
N. H. J. M.

Isolation of Crystalline *dl*-**Glyceraldehyde from a Syrup formed by the Oxidation of Glycerol.** Edgar J. Witzemann (*J. Amer. Chem. Soc.*, 1914, **36**, 2223—2234).—The syrupy product

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obtained by the oxidation of glycerol with hydrogen peroxide in presence of ferrous sulphate (Fenton and Jackson, T., 1899, ??, ??) contains dl-glyceraldehyde. This was established by converting the aldehyde into the diethylacetal and recovering pure dl-glyceraldehyde from the latter by hydrolysis with 0·1 N-sulphuric acid.

L.

Crystallised l-Mannose. W. ALBERDA VAN EKENSTEIN and BLANKSMA (*Chem. Weekblad*, 1914, **11**, 902).—A yield of l·? l-mannose can be obtained by hydrolysis of the cyanohydrin l-arabinose, isolation of mannonolactone from the mixture of ? nonic acid and l-gluconic acid, and reduction with sodium amalgam. To crystallise the sugar, it is converted into the phenylhydrazone, then regenerated by the action of benzaldehyde. After several days the resulting syrup crystallises, and on recrystallisation from alcohol ? colourless crystals, m. p. 132°. It exhibits mutarotation, the ? rotation being $[a]_D +14°$, and the final rotation $[a]_D \cdot 14$, in close agreement with the corresponding constants for d-mannose.

A. J. ?

Preparation of Raffinose. C. S. HUDSON and T. S. Har (*J. Amer. Chem. Soc.*, 1914, **36**, 2110—2114).—During a study of hydrolysis of raffinose by enzymes, a large quantity of the ? was required. A method for its preparation was therefore devised ? is superior to any of those hitherto recorded.

Cotton-seed meal is extracted with water, the aqueous ? treated with basic lead acetate and filtered, and the filtrate treated ? hydrogen sulphide to remove excess of lead, and again filtered little sodium hyposulphite is added to prevent development of ? and the solution is boiled under reduced pressure until it forms a syrup containing about 25% of water. Barium hydroxide is now ? and the barium raffinosate is powdered and washed with methyl ? The barium compound is suspended in water and carefully decomposed with 50% phosphoric acid, so that the solution is exactly neutral at end of this process. After filtration, a little sulphuric acid is added to remove the last traces of barium, and the solution is again ? treated for a few minutes with eponite (a form of vegetable charcoal) filtered, and concentrated in a vacuum to a syrup containing ? of water. A small quantity of alcohol containing 0·3% of water is added, and the mixture is seeded with crystals of raffinose and and left at 0° to crystallise. The crystalline mass is triturated with 75% alcohol, filtered, and washed with alcohol of the ? strength until the washings are colourless. A yield of 4—5 d weight of cotton-seed meal employed may thus be obtained ? colourless raffinose crystals. The product may be further purified recrystallisation.

V. ?

The Solubility of Nitrocellulose in Mixtures of Ether and Alcohol. A. MATTEOSCHAT (*Chem. Zentr.*, 1914, i, 2095; from *Z. ges. Schiess-Sprengstoffwesen*, 1914, **9**, 105—106).—The author measured the solubility of a sample of gun-cotton in mixtures of ether and dry or dilute alcohol. Absolute alcohol and ether is

proportion 1 : 1 make a useful mixture, but with the common diluted spirits the proportion should be, ether to alcohol as 2 : 1 or 3 : 1.

J. C. W.

The Plurality of Amyloses. CH. TANRET (*Compt. rend.*, 1914, **159**, 530–533).—The author has determined the absolute and relative averages of amyloses dissolved by water at different temperatures in different kinds of starch. For the starches used, water, at the same temperature, dissolves very different amounts of amylose. The results are a further proof of the plurality of amyloses as suggested by Fernbach and Roux.

W. G.

Metallic Compounds of Glycine. A. BERNARDI (*Gazzetta*, 1914, **44**, ii, 257—260).—The author has investigated the compound prepared by Dessaigne (*Annalen*, 1852, **82**, 365), examined later by Ley and Kissel (A., 1899, ii, 485), and known as mercury glycine, $(H_2CH_2CO_2)_2Hg$. It is found that the action of alkali on this compound results in no precipitation of mercuric oxide, but in the formation of the compound $CH_2{<}^{NH-}_{CO\cdot O}{>}Hg$. It is suggested that

the latter compound be termed mercuriglycine, and that the former be named mercury aminoacetate.

Mercury aminoacetate, $(NH_2\cdot CH_2\cdot CO_2)_2Hg$, forms tufts of white plates, m. p. 110—111°. *Mercuriglycine*, $C_2H_3O_2NHg$, obtained by the use of the calculated proportion of calcium hydroxide solution on mercury aminoacetate, has m. p. 155° (decomp.), and when treated with sodium thiosulphate liberates sodium hydroxide quantitatively according to the equation :

$H_2O_2NHg + Na_2S_2O_3 + 2H_2O = CO_2H\cdot CH_2\cdot NH_2 + HgS_2O_3 + 2NaOH.$

With mercuric sulphate, mercury aminoacetate forms the double salt, $(CO_2\cdot CH_2\cdot NH_2)_2, HgSO_4, 3H_2O$, decomp. 102°.

Calciglycine, $CH_2{<}^{NH}_{CO_2}{>}Ca$, was also prepared.

T. H. P.

Three Isomeric Ethyl-*sec.*-butylhydroxylamines. LAUDER WILLIAM JONES and LEONORA NEUFFER (*J. Amer. Chem. Soc.*, 1914, **36**, 2202—2208).—Jones (A., 1907, i, 897) has described two isomeric hydroxylamines, namely, β-methyl-a-ethyl- and a-methyl-β-ethyl-hydroxylamine. In the present paper, an account is given of a-ethyl-*sec.*-butyl- and β-ethyl-a-*sec.*-butyl-hydroxylamines which are isomeric with β-ethyl-β-*sec.*-butylhydroxylamine (Bewad, A., 1900, i, 630 ; Bevan and Goulding, T., 1901, **79**, 641).

When hydroxyurethane (carbethoxyhydroxamic) ethyl ether (Jones, 1898, i, 174) is treated with *sec.*-butyl iodide and sodium ethoxide, converted into *carbethoxy-a-ethyl-β-sec.-butylhydroxylamine (hydroxy-butylurethane ethyl ether)*, $C_4H_9\cdot N(OEt)\cdot CO_2Et$, b. p. 105—106·4°/ mm. On hydrolysing this compound with potassium hydroxide, yields *a-ethyl-β-sec.-butylhydroxylamine*, $C_4H_9\cdot NH\cdot OEt$, b. p. 158—89°; its *hydrochloride* has m. p. 94°; the *platinichloride* was prepared and analysed.

By the action of *sec.*-butyl iodide on hydroxyurethane in presence of

potassium hydroxide, *carbethoxy-a-sec.-butylhydroxylamine* (*β-ethyl urethane sec.-butyl ether*), $CO_2Et \cdot NH \cdot O \cdot C_4H_9$, b. p. 116—117 27 mm., is produced, and this, on being treated with ethyl iodide and sodium ethoxide, is converted into *carbethoxy-β-ethyl-a-sec.-butyl hydroxylamine* (*hydroxyethylurethane sec.-butyl ether*),

$$C_4H_9 \cdot O \cdot NEt \cdot CO_2Et,$$

b. p. 86·5—87°/30 mm. The latter compound, on hydrolysis, forms *β-ethyl-a-sec.-butylhydroxylamine*, $NHEt \cdot OC_4H_9$, b. p. 93·5—94°; its *hydrochloride* is deliquescent; the *platinichloride* forms deep yellow crystals.

When carbethoxy-a-sec.-butylhydroxylamine is heated with potassium hydroxide, it is converted into *a-sec.-butylhydroxylamine*, $NH_2 \cdot OC_4H_9$, b. p. 85·5°; its *hydrochloride* has m. p. 54·7—55°, and the *platinichloride* forms deep yellow crystals.

The carbethoxyhydroxylamines described in this paper are liquids with a characteristic odour; they do not reduce ammoniacal silver nitrate or Fehling's solution. a-sec.-Butylhydroxylamine, the ethyl-sec.-butylhydroxylamines have a characteristic amine odour; they reduce ammoniacal silver nitrate in the cold and Fehling's solution when heated.

E. G.

Some New Hydroxyurethanes and Chromoisomeric Silver Salts of Their Acyl Derivatives. LAUDER WILLIAM JONES and RALPH OESPER (*J. Amer. Chem. Soc.*, 1914, **36**, 2208—2227). The experiments described in this paper were undertaken with a view to the preparation of mixed oximinocarbonic esters, $OR \cdot C \cdot NOR'$. Several new carbalkyloxyhydroxamic acids (hydroxyurethanes) have been obtained and their benzoyl esters studied. The silver salts of some of these benzoyl esters were obtained in two isomeric modifications, white and yellow, which are mutually transformable; methyl, ethyl, and *iso*propyl compounds yield only yellow salts, but *iso*butyl, *iso*amyl, and benzyl compounds furnish both modifications. When treated with alkyl haloids, these silver salts yield derivatives in which the alkyl groups are attached to nitrogen instead of oxygen, and for this reason the desired acyl derivatives of the oximinocarbonic esters could not be obtained.

Carbomethoxyhydroxamic acid, $OH \cdot NH \cdot CO_2Me$, was obtained as a thick, yellow oil by the interaction of methyl chloroformate, hydroxylamine hydrochloride, and potassium carbonate. The *benzoyl ester*, $OBz \cdot NH \cdot CO_2Me$, m. p. 82°, forms white needles; its *silver salt*, $OBz \cdot NAg \cdot CO_2Me$, has m. p. 149—150°.

When the silver salt of the benzoyl ester of carbethoxyhydroxamic acid (Jones, A., 1898, i, 174) is heated, it becomes white at 156—159° then darkens rapidly, and melts at 174° (decomp.). The action of ethyl iodide and *iso*amyl iodide on this salt has already been described (this vol., i, 505). By the action of benzoyl chloride on the silver salt of carbethoxyhydroxamic acid or by the action of ethyl chlorocarbonate on the silver salt of dibenzhydroxamic acid, the dibenzoyl derivative of carbethoxyhydroxamic acid (A., 1898, i, 174) is produced.

Carbopropoxyhydroxamic acid, $OH \cdot NH \cdot CO_2Pr$, was obtained as a thick, colourless oil. The *benzoyl* ester yields a *silver salt*, as

—145°, forming yellow needles which do not become white when ... . By the action of benzoyl chloride on this silver salt, the ..... derivative, $OBz \cdot NBz \cdot CO_2Pr$, m. p. 78—89°, is produced, ... crystallises in cubes. When the silver salt is treated with ethyl ..., the N-*ethyl* derivative, $OBz \cdot NEt \cdot CO_2Pr$, is obtained as a pale ... oil, and is hydrolysed by hydrochloric acid with formation of ... hydroxylamine hydrochloride.

...butoxyhydroxamic acid, $OH \cdot NH \cdot CO_2 \cdot C_4H_9$, is a colourless ... The *benzoyl* ester, m. p. 43—44°, yields a yellow *silver* salt which, ... heated at 80—83°, is converted into a white modification, and ... p. 158°. The N-*ethyl* derivative, $OBz \cdot NEt \cdot CO_2 \cdot C_4H_9$, is a ... yellow oil.

...iscamyloxyhydroxamic acid, $OH \cdot NH \cdot CO_2 \cdot C_5H_{11}$, is a viscid, pale ... oil. The *benzoyl* ester, a colourless oil, furnishes a yellow *silver* ... which becomes white at about 75° and melts at 141—142°. When ... salt is treated with benzoyl chloride, the *dibenzoyl* derivative, ... $NBz \cdot CO_2 \cdot C_5H_{11}$, m. p. 69—70°, is produced. The N-*ethyl* ... ture. $OBz \cdot NEt \cdot CO_2 \cdot C_5H_{11}$, is a pale yellow oil which yields ... hydroxylamine on hydrolysis.

...toxyloxyhydroxamic acid, $OH \cdot NH \cdot CO_2 \cdot CH_2Ph$, has m. p. 65°. ... *benzoyl* ester, m. p. 109—110°, yields a *silver* salt, m. p. 150—151°, ... exists in yellow and white modifications. The N *ethyl* derivative, ... $NEt \cdot CO_2 \cdot CH_2Ph$, is a pale yellow oil.

E. G.

Syntheses in the Fluorene and Bisdiphenylene-ethylene ... GONZALO GALLAS (*Anal. Fis. Quim.*, 1914, **12**, 112—131).— ... Dinitrofluorenone condenses with 2 : 7-dinitrofluorene at 160° in ... presence of zinc chloride to form 2 : 7 : 2′ : 7′-tetranitrobisdiphenyl-... ethylene, which on reduction by means of tin and hydrochloric ... yields the corresponding *tetra-amino*-compound, colourless, silky ... m. p. 250° (decomp.). The acid solution develops a blue ... ration with oxidising agents.

G. D. L.

...ction of **Allylthiocarbimide** on Various **Amino**-organic ... compounds. G. ROSSI (*Gazzetta*, 1914, **44**, ii, 264—268).—In the ... ce of a solvent, the interaction of *o*-toluidine and allylthio-... mide at the boiling point of the latter yields, not *s*.-*o*-tolylallylthio-... amide, but *s*.-di-*o*-tolylthiocarbamide and allylamine.

... action of allylthiocarbimide on *o*-aminobenzoic acid is of a more ... cated character and yields allyl cyanide, hydrogen sulphide, ... dioxide and 3-nitrophthalanilide:
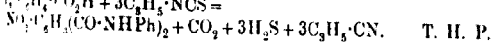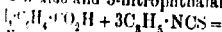
$C_6H_4 \cdot CO_2H + 3C_3H_5 \cdot NCS =$
$NO_2 \cdot C_6H_3(CO \cdot NHPh)_2 + CO_2 + 3H_2S + 3C_3H_5 \cdot CN.$ T. H. P.

Benzoylations in Ether Solution. WILLIAM M. DEHN and ALICE ... (*J. Amer. Chem. Soc.*, 1914, **36**, 2091—2101).—In an earlier ... (Dehn, A., 1912, i, 833) an account was given of the action of ... chloride on various bases in solution in dry ether. Similar ... ments have now been carried out with benzoyl chloride and it ... been found that, as with acetyl chloride, a mixture of the hydro-... and acyl chloride additive compound of the base is pre-

cipitated. In some cases, these precipitates are contaminated with the
original bases or with their benzoyl derivatives. All the benzoyl
chloride additive compounds are dissociated by water and many of
them are unstable towards heat. The additive compounds of
primary and secondary bases can generally be prepared by adding
hydrogen chloride in ether or toluene solution to solutions of the
benzoyl derivatives; the hydrochlorides of benzanilide, o- and p-
tolylbenzamide, and a-naphthylbenzamide, however, could be
obtained in this way,

*iso*Butylamine yields a mixture of its hydrochloride with the
*iso*butylbenzamide. The precipitate obtained with *iso*amylamine,
m. p. 201° and consists of *isoamylbenzamide hydrochloride*, *iso*-
amylbenzamide is an oil, b. p. 310—315°. Aniline gives a precipitate
containing benzanilide and benzanilide hydrochloride. *p*-Toluidine
yields *p*-tolylbenzamide and *p-tolylbenzamide hydrochloride*, which,
and *m*-toluidine and a-naphthylamine afford mixtures of the hydro-
chloride of the base, the benzamide, and the additive compound.
Phenylhydrazine gives a precipitate consisting of phenylhydrazine
hydrochloride, and benzoylphenylhydrazine and its *hydrochloride*.
Carbamide furnishes the additive *compound*, $CO(NH_2)_2, BzCl$ =
209° (decomp.).

Diethylamine and methylaniline yield precipitates of *N*-
diethylbenzamide hydrochloride and phenylmethylbenzamide hydro-
chloride respectively. Piperidine furnishes *benzoylpiperidine hydro-
chloride*, which forms white, hygroscopic needles. Benzylethylamine
gives *benzylethylbenzamide hydrochloride*; *benzylethylbenzamide* has
218°/29 mm.

Additive *compounds* were also obtained with triethylamine,
*iso*amylamine, dimethylaniline, diethylaniline, antipyrine, quinoline,
pyridine, and a-picoline.   J. J.

Copper Lakes of Eosin. HARVEY NICHOLAS GILBERT (*J. Ind.
Chem.*, 1914, 18, 586—618).—An investigation has been made of an
eosin copper lake with the object of ascertaining whether the substance
is a definite compound or merely an adsorption complex consisting of
copper hydroxide with the eosin adsorbed in approximately equal
amount. It is shown that copper hydroxide, when treated with dilute
solutions of eosin in varying quantities, exhibits the typical adsorption
curve, and there is no indication of a chemical compound. The
amount of eosin taken up is about one-tenth of the amount
required to form copper eosinate. Similar adsorption curves were
obtained when magnesium oxide was shaken up with various eosin
solutions. The composition of the copper lake produced by the
interaction of copper sulphate and sodium eosinate was studied, and
was found that the precipitate contained an excess of copper in all
cases where an excess of copper salt was employed. It was also
possible to synthesise lakes from copper hydroxide and eosin which
behaved like the original lake. These lakes could be brought into
colloidal solution, and all behaved similarly, although the ratio of
copper to eosin varied from two molecules of copper to one of eosin to
one molecule of copper to two of eosin. The amorphous lake has a

.... into crystalline copper eosinate. The properties of the
.... lake differed entirely from those of the crystalline substance.
...... decomposition of the lake in aqueous suspension by means of
...... showed that the eosin was set free from the lake by the greater
...... action of the copper hydroxide for the anions of certain salts.
...... anions are adsorbed by the copper hydroxide setting free the
...... eosin. The order of the decomposition, due to these adsorbed
...... is the same as is found for other cases of adsorption :
$>$Br$>$Cl$>$NO$_3'$. The decomposition of the lake by aqueous alcohol
...... aqueous acetone is similar to that of ether and may be explained in
...... same way as due to the preferential adsorption of anions. The results
...... indicate that the lake, produced by the action of an aqueous
...... solution of sodium eosinate on a solution of copper sulphate, does not
...... consist of copper eosinate, although the copper and eosin are present
...... equivalent quantities. The lake consists of copper hydroxide, which
...... the method of formation contains an equivalent amount of
...... adsorbed eosin. A colorimetric method for the estimation of eosin is
...... used, which consists in preparing a solution of cobalt nitrate of
...... exactly the same tint as a solution of eosin containing 0·00125 gram
...... litre. Such a cobalt solution contains 17·84 grams of the nitrate
...... litre. The method of estimation consists in diluting the given
...... solution until it has exactly the same tint as the cobalt standard.

J. F. S.

p-Aminobenzaldehyde and Aniline. G. ROSSI (*Gazzetta*, 1914,
n, 261—263).—The interaction of *p*-aminobenzaldehyde and
...... aniline yields *p*-aminobenzylideneaniline, which crystallises in
...... canary-yellow needles, and forms a *picrate*, brick-red
...... exploding violently at 150°, and, when treated with ethyl
...... *ethyl aminobenzylideneaniline*, NHEt·C₆H₄·CH:NPh, red
...... decomp. 150°.
T. H. P.

Oxidation of the Nopinine of Spanish Oil of Turpentine.
ANTONIO MADINAVEITIA (*Anal. Fís. Quim.*, 1914, **12**, 259—264).—
...... on oxidation with potassium permanganate in alkaline solution
...... nopic acid in conformity with the observations of Baeyer and of
...... (A., 1907, i, 936), and in opposition to the statements of
...... and Fernández (this vol., ii, 78).
G. D. L.

Volatile Oil of Calycanthus floridus. EMERSON R. MILLER,
W. TAYLOR, and M. H. ESKEW (*J. Amer. Chem. Soc.*, 1914, **36**,
.... —2187).—The material used for this investigation consisted of the
...... of *Calycanthus floridus*, collected after the leaves had fallen.
...... were cut off just above the ground, freed from any remaining
...... allowed to dry in the air, and submitted to distillation with steam.
Three samples of oil were obtained at different times in yields of
...... 0·25%, and 0·39%; the small, young plants gave the best yield.
...... samples were pale yellow, soluble in all proportions in 90% alcohol,
...... furnished the following constants: D₂₅° 0·9209, 0·9161, 0·9136;
...... a 100 mm. tube), +2·85°, +2·84°, +6·6°; n_D²° 1·4675, 1·4713,
...... saponification number, 12·5, 14·40, 16·6; saponification

number after acetylation, 75·1, —, 65·7. Calculating the borneol and esters as borneol and bornyl acetate, the oils contained (1) 5·04%, and 5·81% of bornyl acetate, and samples (1) and (3) contain 18·44% and 14·46% of borneol respectively. Samples (1) and (3) contain 35—36% and 69—71% of cineole. Besides borneol, bornyl acetate, cineole, the oil contained d- and l-α-pinene, salicylic acid, one or two esters other than bornyl acetate, and probably linalool and sesquiterpenes.

E. G.

Oils of the Coniferæ. II. The Leaf and the Twig and Bark Oils of White Fir. A. W. Schorger (J. Ind. Eng. Chem., 1913, 5, 809—810). Compare this vol., i, 1134).—The leaves and twigs of white fir, Abies concolor, yield from 0·029 to 0·272% of oil having D^{15} 0·8720—0·8777, $n_D^{?}$ 1·4786—1·4796, $a_D^{20} - 20·11°$ to $- 27·34$; ester number, 1·01—1·81; ester number, 12·52—27·34. The bark has 0·095% of oil having D^{15} 0·8702—0·8767, n_D^{15} 1·4785—, $a_D^{20} - 20·15°$ to $- 20·95°$; acid number, 0·87—1·22; ester number, 6·43—6·88. The composition of the oils was found to be as follows:

	Leaf and twig oil.	Bark.
Furfuraldehyde	trace	...
l-α-Pinene	12	9
l-Camphene	8	...
l-β-Pinene	42	...
l-Phellandrene	15	Dipentene 12
Ester, as bornyl acetate	6·5	...
Free borneol	9·5	...
"Green oil"	3	...
Loss	4	...

W. P. S.

Oil of Black Sage. Charles E. Burke and Charles C. Scalione (J. Ind. Eng. Chem., 1914, 6, 804—806).—Black sage (Salvia Stachyoides) from Southern California yielded 0·9% of an oil, D^{15} 0·8979, [a] 24·4°, n_D 1·4729; acid number, 2·2; ester number, . The oil had the following composition: pinene, 6·0%; cineole, 30% dipentene, terpinene, etc., 25·0%; thujone, 8·0%; camphor, 22% resinous substance, 5·0%.   W. P. S.

Essential Oil of Argentine Mint (Bystropogon Mollis Kth). Adolfo Doering (Bol. Acad. Nac. Ciencias Cordoba, 1913, 18, 379—391).—The essential oil forms about 0·4%, of the plant, and not depositing crystals of menthol at 12°, has D 0·918—0·920 and distils chiefly at 210°. As much as 2·5% of furfuraldehyde are present, and is removed by means of permanganate. Free acid amounts to about 0·7%, and phenols are present in traces. Menthol appears to be absent. The terpenes have not so far been characterised.

G. D. L.

Optical Activity of Cinnamein. L. Rosenthaler (Chem. Zentr., 1914, ii, 36—37; from Schweiz. Apoth.-Zeit., 1914, 52, 273—276).— The rotations of the cinnameins isolated from genuine and false balsams and from some artificial products have been measured in alcoholic and ethereal solutions. The majority of the extracts of genuine balsams had a small dextrorotation. In addition,

...in content was determined, as well as the saponification number ...balsam and of the cinnamein which was isolated from it.

J. C. W.

Synthetic **Caoutchouc.** I. I. ANDRÉEV (*Chem. Zentr.*, 1914, ii, ...326, from *Ber. St. Petersburg Polytech. Inst.*, 1913, **21**, 313—368). An apparatus is described, with diagrams, in which turpentine may ...composed by means of an electrically heated platinum wire, and ...converted into isoprene. The addition of carvene, dipentene, or ...atic hydrocarbons is found to improve the yield of isoprene.

J. C. W.

The **Gitalin Question.** L. ROSENTHALER (*Chem. Zentr.*, 1914, ii, ...from *Schweiz. Apoth.-Zeit.*, 1914, **52**, 349—350).—The author ...with Kiliani (this vol., i, 857) that gitalin is a mixture. He ...separated it into a fraction which forms a hydrate and one which ...not, and has isolated a crystalline substance which is physiologically ...active, and seems to differ from any known constituent of digitalis.

J. C. W.

Dimethylpyrone Hydrochloride. H. N. K. RORDAM (*Oversigt. ...ska Vidensk. Selskabs. Forhandl.*, 1914, 243—262).—The ...stigations which have hitherto been carried out have not made it ...ain whether dimethylpyrone hydrochloride acts as a true salt in ...ous solution, or whether it is resolved into the components dimethyl. ...one and hydrochloric acid. In order to decide the question, the ...hor has determined the concentration of the chloride ion in solutions ...varying strength, by measuring the potential of the electrode: ...solid Hg_2Cl_2, solution of dimethylpyrone hydrochloride, against ...N-calomel electrode; similar measurements were made with ...ous solutions of hydrochloric acid. The equivalent conductivities ...all the solutions were also measured, and on plotting the values of ...chloride ion concentrations (abscissæ) against the equivalent ...activities (ordinates) it is found that the curve for dimethylpyrone ...rochloride lies below that for hydrochloric acid, both curves ...reaching the **same** value for infinite dilution. The conclusion is ...fore that dimethylpyrone exists as a true salt in solution; it is ...drolysed to some extent, the hydrolysis constant being 0·63, and the ...ciation constant of dimethylpyrone as base is calculated to be ...10^{-9} (compare Walden, A., 1902, i, 168). T. S. P.

Solanine-s. VIII. **Nature of the Glucosidic Condensation** Solanine-s; **Glucosides in General.** GIUSEPPE ODDO and ...LLO CEBARIS (*Gazzetta*, 1914, **44**, ii, 181—190. Compare this vol., ...14).—The hydrolysis of solanine-s from *Solanum sodomaeum* yields ...idine-s, d-galactose, dextrose and d-aldomethylpentose:

$$C_{45}H_{75}O_{15}N_s, H_2O = 2C_{18}H_{31}ON + C_6H_{12}O_6 + C_6H_{12}O_6 + C_5H_{12}O_5,$$

...molecule of water of crystallisation sufficing for the decomposition. ...ine-s does not react with phenylhydrazine or hydroxylamine; ...her, the only oxygen atom of solanidine-s is hydroxylic, and the ...gen is present in the form of the imino-group in both compounds.

From these results, the structure of solanine-s and the matter in which water is added to it on hydrolysis are represented thus:

$$
\begin{array}{cccc}
\text{H} & \text{O} & & \text{H} \\
\text{NH:C}_{18}\text{H}_{27}\text{O} \quad \text{—CH·O} & \text{CH} & \text{O·CH} & \text{O·C}_{6}\text{H}_{13} \\
\quad \mid & \mid & \mid & \\
[\text{CH·OH}]_4 & [\text{CH·OH}]_4 & [\text{CH·OH}]_4 & \\
\mid & \mid & \mid & \\
\text{CH}_2\text{·OH} & \text{CH}_3 & \text{CH}_2\text{·OH} &
\end{array}
$$
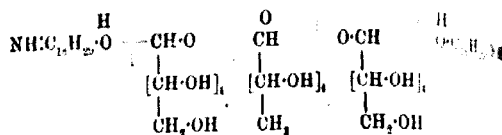
Solanidine.   Dextrose. Methylpentose. d-Galactose.

The results obtained by Oddo and Mameli (A., 1904, i, 28 ... ... acetals prepared from dichloroacetaldehyde hydrate are utilised elaborating a theory to explain the synthesis of solanine from its constituents.   T H ?

Solanine-s. IX. Solanidine sodomaeum and Some of its Products of Disintegration. GIUSEPPE ODDO AND MARCELLO (or rea (*Gazzetta*, 1914, 44, ii, 191—208).—*Solanidine ether,* (NH:C H. obtained by the action of hydrochloric acid on solanidine in alcoholic solution, crystallises in needles, m. p. 176—177°, [a]ₚ –14 5 in benzene, and has the molecular weight 373—425 in freezing benzene, or 248—259 in freezing acetic acid, the calculated value being ... When its alcoholic solution is poured on to concentrated sulphuric acid, a yellow ring, changing to orange, forms at the surface of separation. When treated with nitrous acid, the ether yields a compound, [N(OH)₂·C₁₈H₂₉N·O·C₁₈H₂₉N]₂N·OH, 2 mols. of the ether reacting with 3 mols. of the acid, with elimination of H. This compound forms pale reddish-yellow needles, m. p. 224—5 (decomp.). It gives neither a blue coloration with diphenylamine nor the characteristic reaction of nitroso-compounds with Liebermann's reagent. When treated with acid or alkali, it yield solanidine etc.

The compound described as azosolanidine (A., 1911, i, 671) is found to have the composition C₇₂H₁₁₆O₉N₈[= 4(C₁₈H₂₁ON,HNO₂) –3H₂O] When treated with hydrochloric acid it gives *dihydrosolanidine* C₁₈H₃₃Cl (l), m. p. 113°, and another *compound,* m. p. 130°, which appears to be a chlorinated alcohol, C₁₈H₃₃OCl.

No definite compounds could be separated from the products of action of energetic dehydrating or oxidising agents on solanidine.
                                                                T H

Action of Nitrous Acid on Amines. Behaviour Towards Tropigenine and Granatoline. I. GIUSEPPE ODDO and MARCO CESARIS (*Gazzetta*, 1914, 44, ii, 209—227).—From the results of investigations on the action of nitrous acid on solanine-s and solanidine (compare preceding abstract), the authors draw the conclusion that action of nitrous acid on a primary or secondary amine results in formation of the corresponding nitrite, NHR¹R²,HNO₂, which undergoes transformation into an *as*-dihydroxyhydrazine derivative NR¹R²·N(OH)₂. The further decomposition of the latter varies with the nature of the radicles present, and may follow one or other of three types, which have been named : (1) *Anazoic.* In this ammonium nitrite yields nitrogen and water ; primary amines, etc.

and an alcohol, and secondary amines, nitrogen and either alcohols, or, if $R^1 = R^2$, a single alcohol. (2) *Diazoic.* Here, ammonium nitrite yields nitrosoamine, $NH_2 \cdot NO$, or *isonitrosoimide*, NOH; primary amines give nitrosoamines, $NHR \cdot NO$, or diazohydrates, $R \cdot N:N \cdot OH$, and secondary amines, true nitroso-compounds, $R_2 N \cdot NO$. (3) *Cyclazoic,* which either gives stable azocyclic compounds or ψ-nitroso-compounds, such as $\begin{smallmatrix} C_8H_{14} \\ CO \end{smallmatrix} >C< \begin{smallmatrix} N \cdot OH \\ NH \end{smallmatrix}$, from camphor nitrite, or results in the opening of the nucleus and formation of *allo*nitroso-compounds, for instance, *allo*nitroso-oxindole $C_6H_4 <\begin{smallmatrix} CH(NO) \\ NH \end{smallmatrix}> CO$, from ψ-nitroso-oxindole,

$$C_6H_4 \Big\langle \begin{smallmatrix} CH \\ CO \\ N \end{smallmatrix} \Big\rangle N \cdot OH.$$
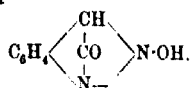
A true dihydroxyhydrazine derivative is obtained by the action of nitrous acid on the ether of solanidine-*s* (*loc. cit.*). With the compounds obtained from solanine-*s* and solanidine-*s*, the complete elimination of the nitrogen by the action of acids shows that in these cases the action of nitrous acid proceeds immediately to the cyclazoic stage. Since the sole difference between solanidine-*s* and its ether consists in the presence of a hydroxyl group in the former, it has been thought desirable to study the action of nitrous acid on tropigenine and granatoline, which are saturated, alicyclic, iminic, alcoholic bases of similar structure. In aqueous solution faintly acidified with acetic acid, tropigenine yields the corresponding nitrite at the ordinary temperature. At the temperature of a boiling-water bath, however, reaction yields a compound which has the composition, but none of the properties of the true nitroso-compound (I) and is regarded as the oxidic ψ-nitroso-compound (II):

$$\begin{smallmatrix} CH_2 \cdot CH & \text{---} & CH_2 \\ | & N \cdot NO & CH \cdot OH \\ CH_2 \cdot CH & \text{---} & CH_2 \\ & (I.) & \end{smallmatrix} \qquad \begin{smallmatrix} CH_2 \cdot CH & \text{------} & CH_2 \\ | & N \cdot N(OH) \cdot O \cdot CH \\ CH_2 \cdot CH & \text{------} & CH_2 \\ & (II.) & \end{smallmatrix}$$
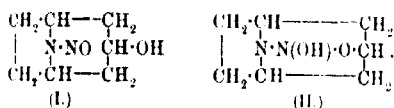
This compound is accompanied by two others in small proportions, the less abundant having the properties of the hydrate of a true nitroso-compound, that is, of the intermediate dihydroxyhydrazine derivative. The interaction of granatoline hydrochloride and silver nitrite gives nitrite of the base, and this in aqueous solution is converted by nitrous acid into the hydrate of the true nitroso-compound (III) (compare Ciamician and Silber, A., 1895, i, 160).

$$\begin{smallmatrix} CH_2 \cdot CH & \text{------} & CH_2 \\ CH_2 & N \cdot N(OH)_2 & CH \cdot OH \\ CH_2 \cdot CH & \text{------} & CH_2 \\ & (III.) & \end{smallmatrix} \qquad \begin{smallmatrix} CH_2 \cdot CH & \text{------} & CH_2 \\ CH_2 & N \cdot N(OH) \cdot O \cdot CH \\ CH_2 \cdot CH & \text{------} & CH_2 \\ & (IV.) & \end{smallmatrix}$$
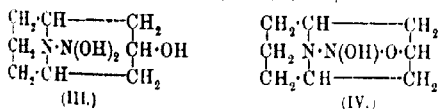
In vacuum, this hydrate gradually loses $1 H_2O$, with formation of the

compound, m. p. 125°, which was obtained by Ciamician and _____
and is the ψ-nitroso-compound (IV).

Tropigenine nitrite, $C_7H_{13}ON,HNO_2$, prepared by the action
silver nitrite on the hydrochloride of the base, forms a ___
crystalline powder, which turns yellow at about 100° and
m. p. 160°.

ψ-*Nitrosotropigenine* (formula II) forms rosettes of white ___
m. p. 195—196°. *Nitrosotropigenine hydrate* has a structure ___
to that of the corresponding granatoline derivative (formula II)
forms white crystals, m. p. about 160° (decomp.).

Granatoline nitrite, $C_{18}H_{13}ON,HNO_2$, forms white needle a
215—216° (decomp.). Nitrosogranatoline hydrate (formula II) ___
white leaflets, m. p. 72—73°. ψ-Nitroso-granatoline (formula II)
m. p. 125°, yields an *ethyl ether*, $C_{10}H_{18}O_2N_2$, white prisms a
65—67°.

T. H.

Direct Attempts to Prepare Ferropyrroles. I. ___

ODDO (*Gazzetta*, 1914, **44**, ii, 268—278).—The author discusses
occurrence of iron and magnesium in hæmoglobin and chloro___
respectively and their derivatives. It is not found possible to ___
organic ferro-compounds containing alkyl or aryl groups, the action
ferric chloride on magnesium ethyl bromide being a chlorina___
action, expressed by the equation:

$$MgEtBr + Fe_2Cl_6 = EtCl + 2FeCl_2 + MgBrCl.$$
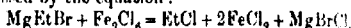
With magnesium phenyl bromide and magnesium benzyl brom___
action of ferric chloride yields diphenyl and dibenzyl respectively
result indicating the intermediate formation of an organo-ferric com___
which then undergoes decomposition, thus:

$$2FePh_2Cl = C_6H_5Ph + FeCl_2 + Fe.$$
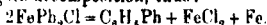
With an organo-magnesium derivative containing a 2-methylin___
residue, the action of ferric chloride gives, however, a more sta___
di-2-methylindolyl ferrichloride, $CH{<}^{C_6H_4}_{CMe}{>}N \cdot FeCl \cdot N{<}^{C_6H_4}_{CMe}{>}$
yellow solid, blackening and contracting at about 130°, and remain
unmelted at 230°.

T. H.

Salts of Acridine, Pyridine, and Quinoline. II. L. H. ___

(*J. Amer. Chem. Soc.*, 1914, **36**, 2101—2110).—It has been shown
the author (A., 1913, i, 92) that when diphenylacridyl chloride
5-phenyl-10-methylacridyl chloride is shaken with nitrobenzene ___
molecular silver, a highly coloured solution is produced which ___
oxygen. It was assumed that these coloured solutions contain ___
acridyl radicles analogous to triphenylmethyl. Evidence has now b___
obtained which proves the accuracy of this assumption, and sem___
unsaturated acridyl radicles and their peroxides have been isol___
The free radicles are dark brownish-red, crystalline substances w___
in solution absorb oxygen from the air to form colourless perox___
and also unite directly with halogens with production of ___
corresponding haloids. They are best prepared by shaking an appro___
solution of a salt, preferably the sulphate, with zinc dust. The ___

... coated with the free radicle and the liquid becomes colourless. ...rating the colourless solution and adding benzene to the moist ..., the benzene dissolves the free radicle, forming a dark red ... On shaking this benzene solution with air, its colour rapidly ...ears and the colourless peroxide soon begins to separate.

...phenylacridyl, $C_{25}H_{18}N$, can be prepared by the method already ...ed or less satisfactorily by the electrolysis of its normal sulphate; ...es when heated and melts at about 185—190°. Molecular weight ...minations have shown that it exists mainly in the unimolecular ...tate. The radicle unites instantly with chlorine to form yellow ...phenylacridyl chloride, and also dissolves slowly in hydrochloric acid ...production of the chloride. The peroxide, $C_{50}H_{36}N_2O_2$, crystallises ...der, pale yellow prisms, and when heated begins to darken at ...190° and melts at 204—207° according to the rate of heating; it ...es slowly in mineral acids with formation of the corresponding ...l salts. When an aqueous solution of diphenylacridyl chloride ...ated with zinc dust, diphenylacridyl is produced together with a ... quantity of **dihydrodiphenylacridine** ("diphenylacridane"), ...N. m. p. 175°, which crystallises in cubes; this substance can ...e prepared by adding zinc dust to a boiling solution of diphenyl-...l in acetic acid.

...e following substances have also been prepared together with ...salts, free radicles, and peroxides, and will be described ...quently: p-chlorophenyl-10-phenylacridol, p-methoxyphenyl 10-...acridol, 2:4-dimethoxyphenyl-10-phenylacridol,phenyl-10-methyl-...ol and phenyl-10-ethylacridol. E. G.

...nines XV. **5-Amino-6 - ethylamino - 2 : 3 - dihydro - 2 -**
...midone and 2 : 8 - Dioxy - 9 - ethyl - 2 : 3 : 8 : 9 - tetrahydro-
...e CARL O. JOHNS and BYRON M. HENDRIX (J. Biol. Chem., 1914, 5 ·50. Compare this vol., i, 440).—2 : 8-Dioxy-9-ethyl-2 : 3 : 8 : 9-...dropurine has been prepared for the purpose of comparing ...perties with those of the methylated compounds, 2 : 8 dioxy-6-...-ethyl-2 : 3 : 8 : 9-tetrahydropurine (A., 1913, i, 1000) and 2-...methyl-9-ethyl-2 : 3-dihydropurine (ibid., i, 1397).

Ethylthiol-6-ethylaminopyrimidine, $NHEt \cdot C <^{N \cdot C(SEt)}_{CH=CH}>N$, b. p.

...11 mm., obtained in almost quantitative yield by heating ...o 2 ethylthiolpyrimidine and 33% aqueous ethylamine at ...in a sealed tube, is converted by boiling with concentrated ...chloric acid and subsequent evaporation to dryness with ...a hydroxide into **6 - ethylamino - 2 : 3 - dihydro - 2 - pyrimidone,** ...N, bluntly pointed prisms, m. p. 218°. The latter, by ...ion with concentrated sulphuric acid and nitric acid (D 1·5) ...70°, yields quantitatively **5-nitro-6-ethylamino-2 : 3-dihydro-2-**
...done, acicular prisms, decomp. 275°, which is converted into ...5-amino-2 : 3-dihydro-2-pyrimidone, stout prisms, decomp. ...by reduction with aqueous ammonia and ferrous sulphate at the ...ary temperature. The base develops in ammoniacal solution a ...blue coloration with phosphotungstic acid and reacts with ...red carbamide at 170—180° to form 2 : 8-dioxy-9-ethyl-2 : 3 : 8 : 9-

tetrahydropurine, $\begin{matrix} N{=}CH{\cdot}C{\cdot}NH{-} \\ | \qquad || \\ CO{\cdot}NH{\cdot}C{\cdot}NEt \end{matrix}{>}CO,$ small prisms, decomp. at 300°.

Etherification of *o*-Hydroxyazo-compounds. V. G. CAUSA and G. FERRARI (*Gazzetta*, 1914, **44**, ii, 228—256. Compare this i, 597, 599, 748).—The *o*-hydroxyazo-compounds derived from α-naphthol and from 10-hydroxyphenanthrene, that is, the 2-arylazo-naphthols and the 9-arylazo-10-hydroxyphenanthrenes, react with methyl or ethyl sulphate in the presence of concentrated alkali solution, thus :

$$OH{\cdot}C_{10}H_6{\cdot}N{:}NAr + SO_2(OR)_2 + KOH =$$
$$OR{\cdot}C_{10}H_6{\cdot}N{:}NAr + OK{\cdot}SO_2{\cdot}OR + \tfrac{?}{?}$$
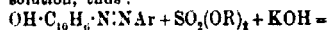
The ethers obtained in this way are well-crystallised, orange or red compounds, which are markedly more soluble in organic solvents, and melt, without decomposing, at lower temperatures the corresponding *o*-hydroxyazo-compounds. They are also decidedly basic than the latter, owing to the intensification of basic properties of the oxygen consequent on etherification. All salts isolated and analysed contain two equivalents of acid, and of the 10-hydroxyphenanthrene series, which could not be got to react as though the base is diacid. To these salts, therefore, attributed one of the two tautomeric structures :

$$X{\cdot}OHR{\cdot}C_{10}H_6(or\ C_{14}H_8){\cdot}N{:}NHXAr\ or$$
$$X{\cdot}OR{:}C_{10}H_6(or\ C_{14}H_8{:}N{:}N{\cdot}NHX)$$
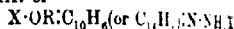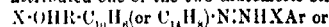
where X represents a halogen atom or a univalent acid res Nascent hydrogen decomposes the ethers into a primary amine NH and an ether of an aminophenol, $OR{\cdot}C_{10}H_6(or\ C_{14}H_8{\cdot}NH_2)$ ethers are extremely resistant to the action of boiling concentrated alkali hydroxide solution, but towards acids their behaviour to The 2-arylazo-1-naphthols are, with some exceptions, highly resist to boiling dilute or concentrated acid, and, when heated, their chlorides suffer loss of hydrogen chloride without decomposition of ether ; on the other hand, the 9-arylazo-10-hydroxyphenanthrene also 2-*o*-methoxy- and 2-*o*-ethoxy-benzeneazo-1-naphthols are hydrolyzed readily by dilute acid, their hydrochlorides being largely decom on heating into the corresponding hydroxyazo-compounds and chlorides of the alkyl radicles of the ethers.

2-*Benzeneazo*-1-*naphthyl methyl ether hydrochloride*, $C_{17}H_{14}ON_2$ forms dark red needles with metallic, green reflection compare Noelting, Grandmougin, and Freimann, A., 1909, i, 442).

2-Benzeneazo-1-naphthyl ethyl ether has m. p. 46° ; Noelting, Grandmougin, and Freimann (*loc. cit.*) gave 44°. Its *hydrochloride*,
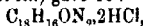
$$C_{18}H_{16}ON_2,2HCl,$$

forms dark garnet-red scales with metallic, golden reflection; *nitrate*, $C_{18}H_{16}ON_2,2HNO_3$, loses nitrous vapours at 47—48° residue melting at 143—145°.

2-*o*-*Tolueneazo*-1-*naphthyl methyl ether*, $OMe{\cdot}C_{10}H_6{\cdot}N{:}N{\cdot}C_6$ crystallises in mammillary masses of orange-yellow needles, 60—61°, and forms a red solution in concentrated sulphuric its *hydrochloride* forms shining, cantharides-green scales. The d

…ing *methyl ether*, $C_{19}H_{18}ON_2$, forms yellow, acicular crystals, m. p. …, *hydrochloride*, metallic golden scales).

m-Tolueneazo-1-naphthol, $OH \cdot C_{10}H_6 \cdot N{:}N \cdot C_6H_4Me$, prepared by the …on of *m*-tolylhydrazine hydrochloride on β-naphthaquinone, forms mamillary aggregates of slender, bright red needles, m. p. 117—118°, …ields a ruby-red solution in concentrated sulphuric acid. The …yl *ether* forms chrome-yellow scales, m. p. 49—50°, and its *hydro*-…de, bronze needles. The *ethyl ether* forms orange-red prisms, … 22°, and its *hydrochloride*, mammillary masses of garnet-red …es.

p-Tolueneazo-1-naphthyl methyl ether forms orange-red needles, … 77—78°, and its *hydrochloride*, minute, brick-red needles. The *ether* forms slender, orange-yellow needles, m. p. 51°, and its *hydrochloride*, deep garnet needles.

as-m-Xyleneazo-1-naphthol, $OH \cdot C_{10}H_6 \cdot N{:}N \cdot C_6H_3Me_2$, prepared by …tion of as-*m*-xylylhydrazine hydrochloride on β-naphthaquinone, …s deep red scales or needles with metallic golden reflection, m. p. … The *methyl ether* forms slender, orange yellow crystals, m. p. …and its *hydrochloride*, metallic, green crystals. The *ethyl ether* …s bright red prisms, m. p. 89°, and its *hydrochloride*, golden scales.

s-Cumeneazo-1-naphthol, $OH \cdot C_{10}H_6 \cdot N{:}N \cdot C_6H_2Me_3$, crystallises in …eaflets or needles with faint golden reflection, m. p. 194—195°, …thyl *ether* forms orange-yellow prismatic needles, m. p. 82—83°, …ts *hydrochloride*, golden-green leaflets. The *ethyl ether* forms red …s, m. p. 64°, and its *hydrochloride*, cantharides-green needles.

p-Chlorobenzeneazo-1-naphthol, $OH \cdot C_{10}H_6 \cdot N{:}N \cdot C_6H_4Cl$, forms bright …iky needles, m. p. 187°. The *methyl ether* crystallises in orange-…e leaflets, m. p. 111°, and its *hydrochloride* in dark green, …e needles. The *ethyl ether* forms orange-red, acicular crystals, …84—85°, and its *hydrochloride*, heavy, cantharides-green plates.

Methoxybenzeneazo-1-naphthyl methyl ether,

$$OMe \cdot C_{10}H_6 \cdot N{:}N \cdot C_6H_4 \cdot OMe,$$
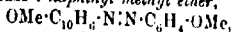
…bright red prisms, m. p. 90—91°, and its *hydrochloride*, greenish-…e needles or leaflets with metallic reflection. The *ethyl ether* forms …red prisms, m. p. 88—89°, and its *hydrochloride*, slender, …arides-green needles.

Ethoxybenzeneazo-1-naphthyl methyl ether,

$$OMe \cdot C_{10}H_6 \cdot N{:}N \cdot C_6H_4 \cdot OEt,$$
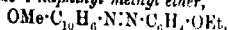
…uses in brick-red needles, m. p. 62°, and its *hydrochloride*, in …arides-green needles. The *ethyl ether* forms bright red needles, …°, and its *hydrochloride*, slender, bronze-green needles.

Benzeneazo-10-methoxyphenanthrene, $OMe \cdot C_{14}H_8 \cdot N{:}NPh$, forms …bright red prisms, m. p. 88—89°, and, on reduction by means of …st and acetic acid, yields aniline and a basic *compound*, which is …bly 9-amino-10-methoxyphenanthrene. The corresponding 10-…y-derivative, $C_{22}H_{16}ON_2$, forms bright red, flattened needles, m. p. …and on treatment with ethereal nitric acid yields benzene-…ium nitrate, 9-nitro-10-ethoxyphenanthrene, and a compound …crystallises in pale red needles, m. p. 249—250° (decomp.), and is …bly a nitro-9-benzeneazo-10-hydroxyphenanthrene ; its behaviour …daction appears similar to that of the methoxy-compound.

The interaction of *as.*-phenylmethylhydrazine hydrochloride
and phenanthraquinone in boiling acetic acid yields neither
benzeneazo-10-hydroxyphenanthrene nor its methyl ether, but
compound which forms pale yellow leaflets, m. p. 221—224°, and
under investigation.

9 - o - *Tolueneazo* - 10 - *hydroxyphenanthrene*, OH·C$_{14}$H$_8$·N:N·C$_6$H$_4$
forms minute, orange-red scales with golden reflection, m. p. 221—222°,
and the corresponding *ethyl ether*, flat, garnet coloured leaf-
m. p. 109°.

9-p-*Tolueneazo*-10-*hydroxyphenanthrene*, C$_{21}$H$_{16}$ON$_2$, forms large
bright red needles, m. p. 169°; its *methyl ether*, dense, bright
needles, m. p. 117°, and its *ethyl ether*, lustrous, bright red
m.p. 158°.

9-o-*Methoxybenzeneazo*-10-*hydroxyphenanthrene*,

$$OH·C_{14}H_8·N:N·C_6H_4·OMe,$$

forms red leaflets with golden reflection, m. p 248—249°, and
ethyl ether, red needles, m. p. 140—141°.   T. H. P.

Aminoazo-compounds. I. CASALE and MARIA CASALE-SEX
(*Atti R. Accad. Sci. Torino*, 1914, **49**, 1199—1209).—The author
have prepared a number of new aminoazo-compounds by coup-
a-naphthylamine with diazonium salts obtained from amines
substituted in the ortho-position. In the products obtained, the
form well crystallised and moderately stable salts with acids
azo-group occurs in the para-position to the amino group of the
naphthalene residue, since 4-o-tolueneazo-1-naphthylamine, for exam-
yields naphthylene-1 : 4-diamine on reduction.

4-o-*Tolueneazo*-1-*naphthylamine*, C$_6$H$_4$Me·N:N·C$_{10}$H$_6$·NH$_2$, crys-
lises in bright red, silky needles, m. p. 95°, and yields intense
solutions in chloroform, benzene or alcohol, and an intensely or
solution in acetic acid; it gives a red coloration with concentrated
a violet one with dilute, sulphuric acid. Its *monoacetyl* deriva.,
C$_6$H$_4$Me·N:N·C$_{10}$H$_6$·NHAc, orange-red needles, m. p. 215° has
derivative, C$_6$H$_4$Me·N:N·C$_{10}$H$_6$·NAc$_2$, brick-red, prismatic par-
m. p. 136°, and *benzoyl* derivative, C$_6$H$_4$Me·N:N·C$_{10}$H$_6$·NHBz,
yellow needles, m.-p. 200°, were prepared. When excess of sod-
nitrite is used in the diazotisation of the o-toluidine, the above com-
pound is accompanied by 4-o-tolueneazo-1-naphthol.

4-o-*Methoxybenzeneazo*-1-*naphthylamine*, OMe·C$_6$H$_4$·N:N·C$_{10}$H$_6$·N
forms tufts of crimson needles, m. p. 184—185°, and gives deep
solutions in chloroform, alcohol or ether, and an intensely violet
in acetic acid. Its *acetyl* derivative, OMe·C$_6$H$_4$·N:N·C$_{10}$H$_6$·NH
forms garnet-red needles, m. p. 203—204°, and its *benzoyl* deriv-
C$_{24}$H$_{19}$O$_2$N$_3$, orange-red needles, m. p. 182°. Here, too, the use
sodium nitrite in excess results in the formation of 4-o-meth-
benzeneazo-1-naphthol (compare Charrier and Casale, this vol.,
748).

4-o-*Ethoxybenzeneazo*-1-*naphthylamine*, OEt·C$_6$H$_4$·N:N·C$_{10}$H$_6$·N
forms groups of vermilion crystals, m. p. 169°; its *acetyl* deriv.,
C$_{20}$H$_{19}$O$_2$N$_3$, red, prismatic needles, m. p. 191°, and its *benzoyl* deriv.,
C$_{25}$H$_{21}$O$_2$N$_3$, tufts of green, silky needles, m. p. 180°.

p-Nitrobenzeneazo-1-*naphthylamine*, $NO_2 \cdot C_6H_4 \cdot N:N \cdot C_{10}H_6 \cdot NH_2$, shining, emerald-green scales, m. p. 174—175°, and gives deeply red solutions in alcohol, benzene, chloroform or ether. Its *acetyl* derivative, $C_{18}H_{14}O_3N_4$, forms tufts of shining, pale green needles, m. p. 200°, and its *benzoyl* derivative, $C_{23}H_{16}O_3N_4$, shining, black plates with red reflection, m. p. 185°.

T. H. P.

Phosphorus Content of Caseinogen. ALFRED W. BOSWORTH and LUCIUS L. VAN SLYKE (*J. Biol. Chem.*, 1914, **19**, 67—71. Compare A., 1913, i, 659).—Additional evidence is adduced to show that caseinogen contains only about 0·7% of phosphorus (compare Rice and Macallum, this vol., i, 443).

H. W. B.

Mode of Action of Urease and of Enzymes in General. DONALD D. VAN SLYKE and GLENN E. CULLEN (*J. Biol. Chem*, 1914, **19**, 141—180. Compare this vol., i, 606).—The consideration of the data already published (*loc. cit.*), and now described in detail, leads to the conclusion that urease destroys urea by means of two successive stages: (1) combination of enzyme and substrate; (2) disruption of the combination, the urea being freed as ammonia and carbon dioxide. This process is formulated in accordance with the law of mass action, and the equation $t = 1/E[1/c \log a_i/(a-x) + x_i/d]$, where a represents the amount of substrate (urea) present per unit volume at the beginning of the reaction, x the amount decomposed in time t, E the enzyme concentration, c the velocity of combination of enzyme and substrate, and d the velocity at which the combination decomposes, giving ammonium carbonate and free enzyme, is found accurately to express all the results thus far obtained.

H. W. B.

Effect of Hydrogen Ion Concentration and of Inhibiting Substances on Urease. DONALD D. VAN SLYKE and GOTTHARD ZACHARIAS (*J. Biol. Chem.*, 1914, **19**, 181—210. Compare Marshall, this vol., i, 606; Armstrong and Horton, A., 1912, i, 594; and the preceding abstract).—The authors have measured the rates of decomposition of urea by urease when the hydrogen ion concentration has been fixed at constant levels by Sörensen's method (A., 1909, i, 861). Changes in the concentration of hydrogen ion have absolutely great and independent effects on the two successive reactions (i) combination with substrate; (ii) decomposition of combined substance by which the enzyme destroys urea. Throughout the range of experimental observation ($P_H = 5·9$ to 8·7), the combining velocity has been found to vary in inverse ratio to the hydrogen ion concentration (the more alkaline the solution the more rapid the combination), but the decomposition by enzyme of the urea combined with it is most rapid in neutral solution and is retarded by either alkalinity or acidity.

In the absence of inhibiting substances such as salts and dextrose, provided the concentration of urea lies between 0·08 and 10%, combination of urease and urea is so quick that it consumes a hardly measurable proportion of the total time, which is almost entirely taken up by the slower decomposition reaction. The maximum rate of

ammonia formation under these conditions is consequently that that of the decomposition reaction, and takes place when the media is maintained at the neutral point. When, however, the reaction reaction is retarded by adding neutral salts or using dilute solutions, it becomes an appreciable factor in the total time consume tion, and the optimum hydrogen ion concentration for the enzyme action is therefore shifted towards the alkaline side effect of hydrogen ion concentration on invertase may also be accounted for as the sum of independent effects on the two separate phases enzyme action.

The effect of the generated ammonium carbonate in retarding action of urease is due chiefly to the alkalinity of the carbonate When a phosphate mixture prevents the ammonium carbonate from affecting the hydrogen-ion concentration, it also prevents effect on the velocity. Neutral salts retard the action of urease interfering with the combination of enzyme with substrate effect is the greater the more dilute the urea solution, and consequently it is especially the decomposition of the last traces of urea that is retarded by neutral salts.

Dextrose retards the enzyme action in the same manner as neutral salts. Alcohol in 30% concentration depresses both phases of the enzyme's action. Both electrolytes and non-electrolytes in more in bimolecular concentration retard the enzyme action in its second phase, namely, the decomposition of urea after it has combined with urease. All these effects can be represented by the general mass action formula for enzyme action already set forth (*loc. cit.*).   H. W. B

Enzyme Action. XI. Some Experiments with Castor bean **Urease.** K. GEORGE FALK and K. SUGIURA (*J. Amer. Chem. Soc.* 1914, **36**, 2166—2170).—In an earlier paper (Falk, A., 1913, ii, it has been shown that castor beans contain a urease. Further experiments have now been made in comparison with the urease of soja beans. It has been found that, under comparable conditions, soja bean preparations hydrolyse much less urea than similar castor bean preparations. The action of acids, bases, and salts on the hydrolysis of urea by castor bean urease has been studied and results have been found similar to those which have been observed in the case of soja bean urease.   E. B

Physiological Chemistry.

Influence of Pituitrin on Respiration. L. B. NICE, J. L. F and R. O. COURTRIGHT (*Amer. J. Physiol.*, 1914, **35**, 194—19) The characteristic effect of pituitary extract on respiration is increase in the depth, followed by a shallowness and a decrease the rate of breathing. In some cases, however, the increase in

of respiration is followed by shallowness and an increase the rate of breathing. The effect of pituitrin on the respiratory mechanism occurs synchronously with that on the circulatory The effect on respiration, however, passes off sooner than on circulation. After a few injections of pituitrin, the respiratory mechanism becomes immune and the characteristic passes are not elicited.

H. W. B.

Normal Level of Blood-Sugar of the Dog. PHILIP A. LEVENE (*J. Biol. Chem.*, 1914, 19, 297—302).—The author finds the concentration of dextrose in the blood of normal dogs, when the animals are free from excitement or pain, is in the neighbourhood of 0·05%, or about one-half to one-third the values usually accepted as normal. Higher figures are obtained after etherisation or when the animal is excited. These higher results are comparable with those hitherto regarded as normal, which may represent varying degrees of emotional hyperglycæmia brought about by the procedure of drawing the blood.

H. W. B.

The Fat of Blood. I. Fat Content of the Blood under approximately Normal Conditions. W. R. BLOOR (*J. Biol. Chem.*, 1914, 19, 1—24).—The author has determined the fat content of the blood, in various circumstances, by his nephelometric method (this vol., ii, 392). In normal circumstances, the fat content of the blood is practically constant, both for the individual and the species, amounting to 0·59 gram per 100 grams of blood. After a fat meal, the fat in the blood increases gradually, reaching a maximum in about six hours. If the thoracic duct is tied, however, an increase in the fat does not occur after feeding with fat. Intravenously injected fat, in quantities up to 0·4 gram per kilo. of body-weight, disappears from the blood within five minutes. When larger amounts are injected, some of the fat remains in the blood for several hours. Apparently the liver is able to withdraw from the blood, and loosely store, a certain amount of fat, but the storage capacity is limited.

Ether and the administration of chloroform produce an increase in the fat of blood only when the animal has previously been well supplied with fatty foods. Ether, however, regularly causes a rise in the fat content of the blood during the narcosis. Loosely stored fat may, therefore, be quickly released by certain drugs, and the sudden flooding of the organism with fat may be a potential source of danger. In the animals that died under the anæsthetic there was observed a rapid and continuous rise in the fat content of the blood during the anæsthesia until death.

H. W. B.

Urea and Total Non-Protein Nitrogen in Normal Human Blood: Relation of their Concentration to Rate of Elimination. FRANKLIN C. MCLEAN and LAURENCE SELLING (*J. Biol. Chem.*, 1914, 19, 31—38).—The authors have determined by Folin's methods

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the relation between the concentration of urea in the b̲l̲o̲o̲d̲ and
its corresponding rate of elimination in the urine. The concentra-
tion of urea and of total non-protein nitrogen in normal human
blood varies within wide limits according to various factors such
as diet, amount of fluid ingested, etc. There is, however, a
parallelism between the concentration of urea in the blood and
the amount excreted in the urine in normal individuals under
average conditions. The elimination of urea is retarded if in-
sufficient water is taken, and the retention of urea is especially
marked in cases of nephritis. A high concentration of urea in
the blood is not necessarily a sign of pathological renal insufficiency
unless associated with a relative decrease in the amount of urea
eliminated in the urine.   H W ?

Proteins of the Blood of Limulus Polyphemus. L. C̲H̲R̲
ALSBERG (J. Biol. Chem., 1914, 19, 77–82).—The proteins of the
blood of Limulus consist almost exclusively of the clot and
(which differs greatly from ordinary fibrinogen) and hæmocyanin.
Hæmocyanin is several times as abundant as the clot in the
Other proteins occur only in minimal amounts. The blood
contains a small amount of nitrogen in non-coagulable form.

The quantity of protein in the blood seems to vary with the
state of nutrition of the animal, diminishing in starvation. The
blood of Octopus contains at least twice as much hæmocyanin as
that of Limulus. The hæmocyanin of Limulus contains
67–68 %.   H W ?

Carbohydrate Metabolism. VII. Influence of Subcutaneous
Injections of Dextrose and of Calcium Lactate on the
Sugar in the Blood and on Tetany after Thyreopara-
thyroidectomy. FRANK P. UNDERHILL and NORMAN R. BLATHER-
WICK (J. Biol. Chem., 1914, 19, 119–126). Compare this vol., i. ?
The hypoglycæmia resulting from thyreoparathyroidectomy seems
to be neither the cause nor the effect of the accompanying tetany,
for although injections of dextrose raise the sugar in the blood
to the normal amount, such injections have little effect on the
tetany. Moreover, the condition of hypoglycæmia precedes that
of tetany. The authors therefore suggest that the removal of the
thyroids and parathyroids gives rise to two distinct effects, one
affecting the mechanism concerned in the maintenance of the sugar
content of the blood at its normal level, thereby causing hypo-
glycæmia, and the other acting on the nervous system, producing
tetany. Calcium appears to be intimately associated with both
effects, for injections of calcium lactate will temporarily restore the
normal sugar content of the blood and also abolish tetany.
                                                            H. W ?

Basal Metabolism and Creatinine Elimination. WALTER
PALMER, JAMES H. MEANS, and JAMES L. GAMBLE (J. Biol. Chem.,
1914, 19, 239–241).—The authors have determined the relation-
ship between basal metabolism (minimum heat production) and

...dual at rest, at least twelve hours after food, and surrounded
...temperature of 30°) and the total mass of active protoplasm
...metabolism of which is represented by the urinary creatinine
...uted on a creatine–creatinine-free diet. The number of
...we per mg. of creatinine varied in eight men from 0·89 to
...average 0·98, whilst in nine women the number ranged from
...to 1·37, average 1·26. Definite conclusions as to the value
...significance of these results are deferred until further observa-
...have been made.   H. W. B.

...eous **Exchange** in **Decerebrate Animals**. CHARLES G. L.
...and T. S. HELE (*J. Physiol.*, 1914, **48**, 428—442). The
...cerebrate animal responds to carbohydrates and proteins in the
...way as the intact animal. The rise in the total metabolism
...wing administration of protein is accompanied by a rise in
...not-protein nitrogen of the blood. The decerebrate animal
...ends to small amounts of amino-acids, such as glycine, which
...a very considerable rise in the protein metabolism. Glycine
...injected into the blood-stream, causes a greater rise in meta-
...than was found by Lusk (A., 1913, i, 123), who adminis-
...this substance *per os.*   S. B. S.

...hibition of **Autolysis** [of **Liver**] by **Alcohol**. H. GIDEON
...LE and GEORGE T. CALDWELL (*J. Biol. Chem.*, 1914, **19**, 57—65).—
...experiments were performed primarily to ascertain what
...ength of alcohol is necessary to preserve specimens of tissue
...fixed for histological purposes. The results show that for the
...plete suppression of autolytic disintegration of liver tissue by
...at the actual strength of alcohol present cannot be safely
...than 90%; between 80 and 90% a slight autolysis may take
...and below 80% alcohol concentration, autolysis is certain to
...place at either room or incubator temperature. Small blocks
...tissue not greater than 5 × 1 × 1 cm. must therefore be placed
...early in at least 50 c.c. of 96% alcohol to prevent autolytic
...ges.

...hen experimenting with finely minced tissues, at least 10 c.c.,
...better, 15 c.c., of 96% alcohol must be added for each gram of
...to ensure effective preservation. When not contra-
...cated, it is best to boil the tissues a short time in the alcohol
...destroy the enzymes.   H. W. B.

...tabolic **Changes** in **Muscular Tissue**. I. The **Fate of**
...tures of **Amino-acids**. S. A. MATTHEWS and C. FERDINAND
...DE (*J. Biol. Chem.*, 1914, **19**, 229—234. Compare Fiske and
...er, this vol., i, 1019).—After repeated injections of a diuretic
...solution into (1) dogs with an Eck-fistula, and (2) eviscerated
...s the urine becomes practically free from ammonia, and con-
...only a small amount of nitrogenous substances. If, now, a
...ture of mixed amino-acids is injected subcutaneously, ammonia
...ars in the urine, followed usually by an increase in the amount
...rea. The conclusion drawn by the authors is that the first

action of the tissues on amino-acids is the formation of urea,
and then the production of urea. The latter change is proved
to be capable of being brought about by the tissues without the
assistance of the liver.　　　　　　　　　　　　H. W. l.

**Reversibility of the Geotropism of Arenicola Larvæ by
Salts.** Sakyo Kanda (*Amer. J. Physiol.*, 1914, 35, 162—176).—
The addition of calcium and magnesium salts in isotonic solution
to sea-water containing the larvæ of *Arenicola* reverses
the normal negative geotropism of these organisms without affect-
ing the normal positive heliotropism. Sodium and potassium
salts, as well as acids and alkalis, have no action on the negative
geotropism, but prevent the appearance of positive heliotropism.
The reversal of the negative geotropism of the larvæ is not an
osmotic effect, but is due to the specific action of the calcium and
magnesium ions.　　　　　　　　　　　　H. W. l.

Purine Enzymes of the Opossum (Didelphis Virginiana).
George T. Caldwell and H. Gideon Wells (*J. Biol. Chem.*,
19, 279—283. Compare Hunter and Givens, A., 1913, i, 171).—In
the tissues of the opossum, enzymes acting on free purines
were found distributed as follows: uricase (uricolytic enzyme)
present only in the liver; xantho-oxydase, present in the liver and
probably in the kidney; guanase, present in all tissues, and
probably not present in any of the tissues, except possibly the
liver.　　　　　　　　　　　　H. W. l.

Excretion of Creatinine by Normal Women. Martha L.
and Elizabeth F. Clark (*J. Biol. Chem.*, 1914, 19, 115—117).—
The analysis of the urines of twenty-six women students on a
creatine- and creatinine-free diet gave the following averages
for daily urinary creatinine: absolute amount eliminated per
gram, varying from 1·71 to 0·53; gram per kilo. of body-weight,
0·015, varying from 0·023 to 0·010; creatinine coefficient (mg.
creatinine nitrogen per kilo. of body-weight), 5·8, varying from
9·8 to 3·5. These figures are considerably smaller than the corre-
sponding figures for normal men.　　　　　　　　H. W. l.

**Some Observations on the Excretion of Creatinine by
Women.** Mary Hull (*J. Amer. Chem. Soc.*, 1914, 36, 2146—2151).
—The urine of several women in normal health has been analysed.
The creatinine output was the chief factor considered, but the
nitrogen excretion in other forms was also determined, and the
results are tabulated. The creatinine varied between 7·31 and
14·97 mg. daily per kilo. of body-weight, the lowest value being
obtained in the case of a corpulent woman who lacked in
physical exercise. These figures are very much lower than the
corresponding values found for men by Long and Gephart (A.,
1912, ii. 961), which ranged from 21·5 to 27·8 mg. per kilo. of
body-weight. It is suggested that this difference may partly
be explained by the lower muscular structure and lower muscular
tone of women.　　　　　　　　　　　　E. G.

Creatine and Creatinine in Starvation. G. GRAHAM and P. POULTON (*Proc. Physiol. Soc.*, 1914, lii—liv; *J. Physiol.*, **48**, compare this vol., i, 228).—The results suggest that traces of creatine only are excreted in starvation of the human subject which has lasted over three days. The excretion did not begin until forty-eight to fifty-eight hours after the last meal. Complications due to the excretion of acetoacetic acid were avoided. S. B. S.

Elimination of Phenolsulphonephthalein in Acute and Chronic Tartrate Nephritis. FRANK P. UNDERHILL and NORMAN BLATHERWICK (*J. Biol. Chem.*, 1914, **19**, 39—56).—The rate of elimination of phenolsulphonephthalein after ingestion may be greatly diminished during the acute stage of nephritis produced in rabbits by the subcutaneous injection of tartrates (A., 1912, ii, 7). In the chronic condition, the excretion of the dye is more rapid, but does not reach the rapidity associated with the normal state. When excretion by the kidney is prevented, the dye is eliminated in the fæces through the bile.

The injection of tartrates does not reduce the excretion of nitrogenous substances in the urine. Although the rate of elimination is undoubtedly diminished, the total amount of waste material excreted is unchanged. A reduced rate of elimination does not necessarily mean that the kidney is not efficient.

It has been observed in these experiments that, contrary to what is previously noted (*loc. cit.*), the glomerulus has been injured as well as the renal tubules. H. W. B.

Volatile Substances of Urine. WILLIAM M. DEHN and FRANK HARTMAN (*J. Amer. Chem. Soc.*, 1914, **36**, 2118—2136).—The characteristic odour of urine cannot be attributed to any of the single substances hitherto detected in it, and it is evident that other compounds must be present. As this subject has not been investigated systematically, the present work was undertaken.

Vapour-pressure determinations of samples of urine, from a few hours to three weeks old, have shown that the variations of the vapour pressure with age are not large, but that in all cases the vapour pressures are lower than those of water at the same temperature.

The largest yields of volatile substances were obtained from urine by treating it with dilute sulphuric acid, leaving it for several days, and then distilling it. The distillates furnished products which were separated into four fractions, namely, acids, phenols, bases, and neutral substances. Of the acids, the principal is benzoic acid, formed by the hydrolysis of hippuric acid; the others comprise hydrogen sulphide, fatty acids up to heptoic acid, and possibly *cyclo*hexanecarboxylic acid. The phenols include *o*- and *p*-cresol, and some higher compounds. The chief bases are trimethylamine and indole; traces of these occur in fresh urine and larger quantities in fermented urine. The neutral substances contribute most largely to the characteristic odour; indications were obtained of the presence of at least four new compounds, including one (see following abstract). E. G.

Urinod, the Cause of the Characteristic Odour of ...
WILLIAM M. DEHN and FRANK A. HARTMAN (*J. Amer. Chem* ...
36, 2136—2146. Compare preceding abstract).—The chara... ...
of urine has been found to be due to the presence ...
C_6H_8O, b. p. 108°/28 mm., a pale yellow oil, slightly ...
water, and possessing a very penetrating, persistent, ...
odour. This substance is readily volatile with ste... ...
potassium permanganate and ammoniacal silver n... ...
cold, and reacts with Millon's reagent, but not with F... ...
tion or solution of alkali picrate. The *dinitro*-deri... ...
78°, forms golden needles. Urinod reacts with semi... ... ...
production of a *compound*, m. p. 254°, which crystal... ...
hexagonal leaflets. When urinod is treated with b... ...
compounds are produced; one of these has m. p. about 11... ...
the other is not melted at 250°. The compound ind... ...
the structure of *cyclo*hexene-4-one, $CO\diagdown\substack{CH_2\cdot CH \\ CH_2\cdot CH}$ ... $\parallel$

quinonoid constitution $CO\diagdown\substack{CH_2\cdot CH_2 \\ CH_2\cdot CH_2}\diagup C$. Urinod does n... ...

in the free state in urine, but exists in a conjugated form ...
liberated by fermentation or by the action of dilute su... ...
It is very toxic, and may have some connexion with ure... ...
                                                      E. ...

The Isolation of the Substance in Butter Fat w...
Exerts a Stimulating Influence on Growth. E. V. M...
and MARGUERITE DAVIS (*J. Biol. Chem.*, 1914, **19**, 2...
Compare Osborne and Mendel, A., 1913, i, 1128).—The ...
stimulating substance present in butter-fat has been is...
saponifying the fat and extracting the soaps formed with ...
ture of olive oil and ether. After removal of the ether, ...
oil was found to have acquired growth-stimulating pr...
which were previously absent. Rats which had ceased t...
on a diet of casein, dextrin, lactose, agar-agar, and salts, w...
addition of ordinary olive oil or of cotton-seed oil, began t...
again when the above olive-oil extract of butter soaps was ...
to the diet.   H. W. ...

Pharmacological Action of Tetra-alkylammonium C...
pounds. I. The Action of Tetramethylammonium Chl...
C. R. MARSHALL (*Trans. Roy. Soc. Edin.*, 1914, **50**, 17—4 ...
detailed account of work published previously (A., 1911, ii, ...

Metabolism of an Isomeride of Xanthine and of so...
Isomerides of the Methylxanthines. SAMUEL GOLDSE...
(*J. Biol. Chem.*, 1914, **19**, 83—104).—The author has studi...
behaviour of various purine derivatives closely related to xa...
and uric acid when injected subcutaneously into ra...
2:8-Dioxytetrahydropurine, an isomeride of xanthine, is exc...
unchanged in the urine, whereas xanthine itself forms all...
and uric acid. Uric acid, when injected subcutane...
eliminated chiefly as allantoin. 2:8-Dioxy-6-methyl-2,8 ...

-ethyl- and 2 : 8-dioxy-6 : 9-dimethyl-tetrahydropurines do not
-- is an increase of urinary allantoin when injected subcutane-
-y into rabbits, which is in accordance with the view that
-thylation is effected only with great difficulty in the body.
-- -ove methylated purines do not produce diuresis.

H. W. B.

Toxicity of Sodium Tartrate. WILLIAM SALANT and C. S.
-- (*Amer. J. Physiol.*, 1914, **35**, 239—264).—The toxic action
-dium tartrate has been observed in rabbits, cats, fowls, and
-- after intravenous and subcutaneous injection and adminis-
-- by the mouth. Comparatively large doses, up to 4 grams
-- -e, may be given with the food to rabbits and fowls without
-- -cing any toxic effect. Larger quantities cause death often
-- a few hours. Sub-acute intoxication is produced by sub-
-- -ous or intravenous injection of small doses, the effects being
-- to the kidney and symptoms of muscular and nervous
-- -ance.

-- state of nutrition of the animal plays a considerable rôle
-- -ermining the extent of intoxication produced by a given dose
-- -ium tartrate. Rabbits fed on carrots are much more
-- -ant than those fed on oats and cabbage or on a milk diet.
-- fatal dose for fasting animals may be barely toxic for those
-- -ll-fed state. Resistance seems to decrease with age.
-- and *l*-Tartrates are found to be equally toxic. H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

Chemical Changes in Vegetable Organisms Undergoing
Fermentation. MARIN MOLLIARD (*Compt. rend.*, 1914, **159**,
-- -514).—Experiments were made on the changes in the sugars and
-- -genous compounds in the pericarp of *Cucurbita maxima* kept
-- -en and in closed tubes for periods of 30, 75, and 150 days.
-- -th the loss of total substance and of reducing sugars soluble
-- -cohol was greatest in the open tubes, whilst the non-reducing
-- -r soluble in alcohol first disappeared in the closed tube; the
-- insoluble in alcohol remained almost the same in the open
-- and were only considerably reduced in quantity in the closed
-- during the last period of the experiment.
-- -hilst the total nitrogen remained about the same, the protein
-- -gen decreased to rather more than half in the open tube and
-- -re than half in the closed tube. The soluble nitrogen (especi-
-- ammonia) increased under both conditions, the increase
-- greater in the closed tube. The amino-nitrogen remained
-- -tant in the open tube, and was doubled in the closed tube,
-- the amide nitrogen disappeared altogether, first in the closed

N. H. J. M.

Relation of Bacterial Transformations of Soil N[...]
to Nutrition of Citrous Plants. KARL P. KELLERMAN (J[...]
Research, 1914, 2, 101—113).—The results of pot experime[...]
which soils from typical orange-growing areas in California [...]
employed showed that an excess of nitrogen as nitrates [...]
the same symptoms of malnutrition as have been observed in [...]
areas throughout the orange belt in California. An exam[...]
of samples of soil from California showed that samples from [...]
vicinity of deteriorating trees are richer in nitrates than [...]
Both the poor and good soils usually contain rather [...]
amounts of insoluble nitrogen, the difference being in the rat[...]
nitrification. In pot experiments it was found that a [...]
of nitrification is obtained by mixing a green crop with [...]
Large amounts of mature straw are to be avoided; small a[...]
of straw may, however, be applied with advantage to [...]
high in nitrates. Ground limestone, in addition, will proba[...]
beneficial.   N. H. J. M.

The Soluble Polysaccharides of Lower Fungi. II. My[...]
galactan, a New Polysaccharide in Aspergillus [...]
ARTHUR W. Dox and RAY E. NEIDIG (J. Biol. Chem. 1914 [...]
235—237. Compare this vol., i, 1038).—*Mycogalactan*, C_6H_1[...]
is obtained from hot aqueous extracts of immature cultur[...]
Aspergillus niger by treatment with alcohol. The dried mate[...]
dissolves in cold water at the ordinary temperature, and w[...]
the solution is immersed in a freezing mixture a transparent g[...]
is formed. It gives a faint blue colour with iodine, which [...]
be due, however, to a trace of impurity. It has a [...]
Galactose is produced by hydrolysis with dilute acid.   H. W. B.

Formation of Hexone and Purine Bases in the Autol[...]
of Glomerella. HOWARD S. REED (J. Biol. Chem. 1914 [...]
257—262. Compare A., 1911, ii, 916).—Autolytic changes occur[...]
in cultures of *Glomerella rufomaculans* result in the prod[...]
ammonia, histidine, lysine, xanthine, and hypoxanthin[...]
indication of the formation of amines could be detected [...]
dried fungous mycelium when incubated with gelatin [...]
liberated lysine.   H. W. B.

β-*p*-Hydroxyphenylethylamine, a Pressor Compound in[...]
American Mistletoe. ALBERT C. CRAWFORD and WALTE[...]
WATANABE (J. Biol. Chem., 1914, 19, 303—304).—The base C,H[...]
previously isolated by the authors (*Jour. Amer. Med. Assoc*[...]
57, 865) from *Phoradendron flavescens* (mistletoe) has [...]
identified by them as β-*p*-hydroxyphenylethylamine.   H. W. B.

Proximate Analysis of Wheat. A. BARBIERI (*Compt*[...]
1914, 159, 431—434).—Twenty kilos. of wheat were washed w[...]
distilled water, and the residue submitted first to maceration w[...]
cold water, then extraction with warm water (50—60°), and fu[...]
with boiling water. The residue from this treatment was su[...]

of the portion passing through was treated with absolute alcohol, finely granular, homogeneous, white flour (*M*) being obtained on filtration. The portion remaining on the sieve was similarly mixed with alcohol, filtered, and the filtrate kept. The aqueous extracts obtained with boiling and warm water were separately concentrated on a water-bath, and then alcohol was added, the precipitates, *a* and *β*, being filtered off. These two filtrates were mixed with those from *M*, and from the residue on the sieve, the alcohol was distilled off, and the aqueous residue (*C*) shaken with chloroform. The filtrates from the first two treatments with water were also shaken with chloroform after concentration. The three separate chloroform extracts so obtained were mixed, and on distilling off the chloroform, the residue, after treatment first with water and then with alcohol, yielded from the second solvent grams of a yellow colouring matter, which was probably a physiological transformation product of chlorophyll. It did not give either the biuret reaction or the reaction for acraldehyde, was insoluble in water, but soluble in benzene, carbon disulphide, or in petroleum. The aqueous layer from *C* was treated with alcohol until a slight precipitate appeared, and then dialysed, and in the dialysed liquid monopotassium phosphate and potassium phosphate were obtained, but no monocalcium phosphate.

The flour *M*, together with the precipitates *a* and *β*, on extraction with ether, gave an oil, of which the major portion was insoluble in acetone, and contained no phosphorus, sulphur, or nitrogen, and the smaller, soluble portion, 8 grams, contained ·1 gram of phosphorus, thus proving the non-existence of fats in the wheat. By incinerating the flour *M*, and also the residue on the sieve, they were found to contain, respectively, 0·30 and 8·62% of insoluble salts, consisting chiefly of calcium sulphate and tricalcium phosphate, but no carbonates.   W. G.

The Organic Phosphoric Acid Compound of Wheat Bran. — R. J. ANDERSON (*J. Biol. Chem.*, 1914, **18**, 425—440. Compare A., 1912, ii, 1205).—The author shows that the organic phosphoric acid compounds obtained from wheat bran by the usual methods are contaminated with oxalates and inorganic phosphates. Purer preparations have now been obtained by precipitation from very little hydrochloric acid with alcohol. Several amorphous barium salts have been prepared; also an amorphous silver salt, which browns very rapidly, and finally turns quite black. These compounds are quite different from the corresponding phytates. Evidence is adduced to show that wheat bran contains several organic phosphoric acids differing so slightly from one another that their separation is very difficult.   H. W. B.

The Organic Phosphoric Acid Compound of Wheat Bran. II. Inositol Monophosphate, a New Organic Phosphoric Acid Occurring in Wheat Bran. R. J. ANDERSON (*J. Biol. Chem.*, 1914, **18**, 441—446. Compare preceding abstract).—Inositol monophosphate is prepared from the hydrochloric acid extract of

wheat bran by treatment with barium hydroxide, filtering the precipitate, and, after removing excess of barium, concentrating in a vacuum and precipitating with alcohol. The substance was purified by means of its insoluble lead salt. After recrystallisation from water, with the addition of alcohol, it was obtained in colourless, star-shaped aggregates of plates or prisms.

Inositol monophosphate, $C_6H_6(OH)_5 \cdot O \cdot PO(OH)_2$, when heated rapidly in a capillary tube, softens at 200°, and decomposes, 201—202°. When slowly heated, it softens at 188°, and melts at 190—191° (decomp.). It is optically inactive. It is very soluble in water, giving an acid solution, but is insoluble in alcohol and the usual organic solvents. In the cold, no precipitate is produced with copper acetate, but on warming the solution, a bluish precipitate separates, which again dissolves completely on cooling. After hydrolysis with sulphuric acid or ammonia in a sealed tube, inositol and phosphoric acid were isolated and identified.

H. W. B.

Is Silica an Indispensable Constituent of Plant Food?
MARSHALL LUNDIE (*S. African J. Sci.*, **9**, No. 10; *Chem. News,* 1914, **110**, 200—202).—Water culture experiments with wheat supplied with the usual nutrients, but without silica. The dry leaves and stems contained, respectively, 1·212 and 0·347 % silica.

Reference is made to a previous experiment, by Hahn, in which wheat grown under similar conditions was attacked by rust, one plant being overrun with the fungus in two days.

It is suggested that whilst silica is not an essential plant food for cereals, it may be of use in enabling the plants to resist attacks of fungoid growth. If this is correct, cereals grown on chalk and basalt soils should suffer less from fungoid attacks than one grown on granite soils, climatic and weather conditions being the same (compare Hall and Morison, *Proc. Roy. Soc.*, 1906, [B], 7, 455).

N. H. J. M.

[**Influence of Zinc, Copper, Manganese and Cerium on the Growth of Wheat.**] J. A. VOELCKER (*J. Roy. Agric. Soc. Eng.*, 1913, **74**, 411—427. Compare A., 1913, i, 1430).—Experiments with wheat grown in pots containing 40 lbs. of soil. Zinc was applied at the rate of 0·01, 0·02, and 0·03% in the form of phosphate, nitrate, and carbonate; copper (0·0025, 0·005, 0·025, 0·05, and 0·1%) as sulphate and carbonate; manganese phosphate and carbonate, and cerium as oxide and sulphate (0·05, 0·025, and 0·005%).

As regards zinc, it was found that the larger amounts of nitrate retarded germination, whilst the other salts were almost without effect on germination and in the earlier stages of growth. Later in June, a toxic effect was shown in the case of the larger amounts of carbonate and phosphate, and especially with nitrate, which caused the tops of the ears to be practically "blind." The final results showed a reduction in the yield of grain, except with 0·01

zinc as nitrate, and, coincidently, a more or less considerable of straw (except with the largest amount of nitrate); with 1% of zinc as nitrate the yield of straw was nearly doubled, the lowest gain, with 0·03% as carbonate, was 29%.   Zinc nitrate and carbonate increased the root development, which very stunted when nitrate was employed.

The conclusions drawn from the copper experiments are that stimulation occurs when the application is between 0·01 and 0·02%; as larger amounts are toxic, and that smaller amounts are without effect.   The greatest gain (straw 79 and grain 62%) was caused with 0·02% of copper as carbonate.   With the beneficial amounts of copper, especially with the sulphate, the roots were very extensive and fibrous as compared with untreated plants.

The results obtained with manganese and cerium were negative, no indications of stimulation or of toxicity being obtained.

N. H. J. M.

Occurrence of Hydrogen Cyanide in Millet and Guinea Corn.
R. Furlong (*Analyst*, 1914, **39**, 430—432).—See this vol., ii, 821.

Occurrence of Methyl Alcohol in Maize Silage. E. B. Hart and R. Lamb (*J. Amer. Chem. Soc.*, 1914, **36**, 2114—2118).— Hart and Willaman (A., 1912, ii, 1205) have found that maize silage contains a small amount (about 0·05%) of methyl alcohol, whereas Browne and Neidig (A., 1913, i, 236) have stated that this alcohol is absent.

Several samples of maize silage have now been examined, and in all cases the presence of methyl alcohol was detected.   As a number of different tests were employed for identifying the methyl alcohol, the possibility is precluded of the reactions being due to some other substance.   E. G.

Lucerne. V. Enzymes Present in Lucerne. C. A. Jacobson and August Holmes (*J. Amer. Chem. Soc.*, 1914, **36**, 2170—2182).— In an earlier paper (A., 1913, i, 151) an account was given of the enzymes present in the seeds of lucerne (*Medicago sativa*).   A comparative study has now been made of the enzymes in (*a*) the dried stems and leaves, (*b*) the fresh stems and leaves, and (*c*) the roots. The following enzymes have been detected.   In (*a*), emulsin and pectinase in large quantities, invertase and protease (peptolytic), and small quantities of amylase and peroxydase. In (*b*), emulsin and pectinase in large quantities, coagulase, peroxydase, and protease (peptolytic), and small quantities of amylase, and invertase.   In (*c*), peroxydase in large amount, coagulase, invertase and pectinase, and small quantities amylase and emulsin.   E. G.

Experiments with Tomatoes. J. A. Voelcker (*J. Roy. Agric. Soc. Eng.*, 1913. **74**, 419—422).—Pot experiments with tomatoes in artificial soil consisting of rotted turf, sand, and limestone, both in its natural state and after being heated in a moist con-

dition at 80—100°. To some pots lithium phosphate (L.
and 0·005%) was added, whilst others received magnesia
amounts that the total magnesia in the soil was raised
to 0·792, 1·188 and 1·584 respectively. The highest amount
magnesia was practically equal to the lime present in the

The effect of heating alone was to raise the yield of
Addition of 0·002 and 0·005% of lithium to the
reduced the yields to 29 and 37% respectively of the
obtained in soil alone. In the heated soils with lithium
were 71 and 14%. So that the toxic effect of the smaller
of lithium was much reduced by heating the soil, whilst
larger amount the toxic action was more marked in the heated

As regards magnesia, the normal soil containing 1·188
an increase of 13% over the unmanured soil, whilst in those
taining 0·792 and 1·584% the yields were respectively
89 and 12%. In the heated soils containing 0·792% of magne
the yield was 31% over that of the unheated soil without
magnesia; with 1·584% of magnesia in the heated soil the yield
was only 22%. Magnesium carbonate gave similar results
oxide.

As compared with wheat, tomatoes are more affected
and magnesium.   N. H. J. M

Comparative Efficiency for Milk Production of the Nitro
gen of Lucerne Hay and the Maize Grain. Effect of Diure
on Milk Secretion.   E. B. HART and G. C. HUMPHREY
J. J. WILLAMAN and A. R. LAMB (J. Biol. Chem., 1914, 19,
Compare A., 1913, i, 151).—Further experiments on heifers
that the nitrogen of lucerne hay is as effective as that of the maize
kernel for the formation of the milk proteins.

Lucerne hay has specific diuretic properties. The increased
renal activity observed when it is employed as a constituent of
food is associated with a corresponding diminution in the
milk. The diuretic stimulus causes in some cases a shrinking
volume of 2·5—2·75 kilos. of milk in a flow of 11·5 kilos. It
has not been ascertained whether salts or specific substances
organic nature in the hay are responsible for the diuretic
                                                  H. W. B

Flavour of Roquefort Cheese.   JAMES N. CURRIE
Research, 1914, 2, 1—14).—During the ripening of Roquefort cheese
considerable amount of the fat is hydrolysed, the chief factor
the hydrolysis being a water-soluble lipase produced by Peni-
cillium roquerforti. The result is an accumulation of the
milk fat, both free and combined.

The peppery flavour of the cheese is due to hexoic, octoic
decoic acids, and their readily hydrolysable salts.
                                                  N. H. J. M

Humic Acids.   BR. TACKE, A. DENSCH, and TH. ARND
Jahrb., 1914, 45, 195—265).—A reply to Gully (Mitt. k. bayr. Moo
kulturanst, No. 5), in which the behaviour of peat towards

...phate, sodium acetate and other salts, calcium oxalate, ...sium and ferric chlorides, and colloidal ferric hydroxide, the ...ation by water of absorbed bases from *Sphagnum* and peat, ...electric conductivity, the iodine reaction, the inversion of ...rose by peat, and the liberation of hydrogen in presence of iron ...f peat, are discussed. The results are opposed to the view that ...ctions are due to colloid adsorption, and not to the presence of ...is.

N. H. J. M.

Selective **Adsorption (by Soils).** E. G. PARKER (*J. Ind. Eng.* ...*m*, 1914, **6**, 831—835).—Soils have not only the power of adsorbing dissolved salts from solution, but also of adsorbing one ...n at a greater rate than the other; the nature of the surface ...the constituents of a soil is such that the cation is adsorbed at ...much greater rate than the anion. The presence of bases ...cium, magnesium, etc.) in solution, after contact of certain ...t solutions with a soil, is not due to direct chemical reaction ...the salt with the silicates of the soil, but to a secondary reaction ...the free acid, resulting from the selective adsorption of the ...ions, with the mineral constituents of the soil. Generally, the ...aller the soil particles, the greater the selective adsorption of ...e cation. The adsorption of the cation increases with the concentration of the solution up to a certain point, and then remains ...actically constant. At very low concentrations the adsorption ...the cation is complete. The presence of other substances may ...may not affect selective adsorption by a soil.   W. P. S.

Occurrence of Aldehydes in Garden and Field Soils. ...RED SCHREINER and J. J. SKINNER (*J. Franklin Inst*, 1914, **178**, ...) 343).—Experiments in which a large number of soils were ...reated with 3% sodium hydroxide, and the extracts, after being ...ated with acid to remove the humic acids, examined for aldehydes. Physiological tests were made with the aldehydes by means ...wheat seedlings, and when possible qualitative tests with ferric ...ride and magenta reagent were made. The soils included ...teen garden and greenhouse soils which had failed to grow ...ed crops, and sixty field soils.

Of the unproductive garden soils, five contained aldehydes; out ...thirty unproductive field soils, nine contained aldehydes; and ...it of the same number of productive soils, three contained ...ehydes.

Aldehydes were found in neutral, acid, and alkaline soils, mostly ...acid soils. No relation seems to exist between the crop being ...wn or the type or texture of the soil and the presence of aldehydes. The presence of aldehyde is not confined to any locality, ...g found as far apart as New York and Mississippi.

The effect of the extracted aldehyde material on the growth of ...at varied from slightly, to very, harmful. Of the extracts in ...ch aldehydes were not found, nineteen were without effect, ...teen were injurious, and fourteen beneficial or slightly so.

N. H. J. M.

Action of Manganese in Soil. J. J. Skinner and I. Sullivan (*U.S. Dept. Agric., Bull.* No. 42, 1914).—The results of experiments in which wheat was grown in an unproductive loam, both without and with addition of manganese (as sulphate, nitrate, carbonate, and dioxide), showed a marked effect when the salt was applied in amounts from 5 to 50 per million. On a productive loam, manganese salts were without effect.

In further experiments on the action of manganese on the growth of wheat in aqueous extracts of soils, and on the oxidising power of the plants, it was again found that there was increased growth and oxidation in unproductive soils; in productive soils there was increased oxidation, whilst the growth was decreased.

Finally, a field experiment is described in which wheat, maize, cowpeas, and potatoes were manured with manganese sulphate (56 kilos. per hectare). It was found that manganese sulphate decreased both the crop and the oxidising power of the soil, which was an acid one.

The conclusion is drawn that the beneficial action of manganese may be due to increased oxidation, resulting in the destruction of injurious products in the soil, whilst the injurious action in the case of good soils may be due to excessive oxidation.

Acid soils, which are unfavourable to oxidation and which do not seem to be benefited by manganese. N. H. J. S.

Sulphur as a Fertiliser. J. A. Voelcker (*J. Roy. Agric. Engl.*, 1913, **74**, 419).—Applications of flowers of sulphur at the rate of 3·36, 6·72, and 13·44 kilos. per hectare, were without effect on mustard, rape, and clover grown in pots. The sulphur was mixed with the last portion of the soil used to fill the pots.
N. H. J. S.

Influence of Sulphur on Soil Acidity. H. Clay Lint (*J. Ind. Eng. Chem.*, 1914, **6**, 747—748).—In order to ascertain the oxidation of sulphur in soils, 100-gram portions of soil were treated with 33 mg. of sulphur (equivalent to 1000 lb. of sulphur per acre-foot), and the moisture content was adjusted at 20%. The acidity of the soils increased gradually, as shown by the Jones calcium acetate method, up to the eighth week, when all the sulphur was oxidised. Sulphur is oxidised more rapidly in heavy clay soils than in sandy loam soils (compare A., 1913, i, 811).
W. P.

General and Physical Chemistry.

...rum of the Oscillatory Discharge in Various Gases. BRUNETTI (*Nuovo Cim.*, 1914, [vi], **7**, i. 390—410).—The ... has investigated the spectra of the oscillatory discharge ... between magnesium electrodes in hydrogen, oxygen, ... and carbon dioxide. The first part of the discharge ... lines of the gas and of the metal of high and low excitation; ... second part, the metallic lines of low excitation remain, and ... accompanied by the bands of the gas and of the compounds ... latter with the metal. The bands start from the positive ... and cease at a distance from the negative one, whilst the ... traverse the whole space between the electrodes, and the ... lines are not found in the regions bordering on the elec ... The first phase of the oscillatory discharge presents, ... those complex phenomena known as a spark; it opens the ... ionising the gas, carries with it occasional particles of the ... and heats the electrodes to redness, being then replaced by ... second phase of the discharge, namely, the arc. In the latter ... a localisation of the seat of emission of the various series ... the principal series originating in a stratum surrounding ... series emitted by the central regions. The heating ... electrodes during this second part of the discharge depends ... thermal conductivity of the surrounding medium; in ... the heating does not last so long as in nitrogen, oxygen, ... dioxide, whilst the discharge is extinguished sooner. The ... change in potential at the electrodes falls off in the adjacent ... for equal magnitudes of the auto induction, the difference ... potential at the electrode is greater in oxygen than in nitrogen, ... least in hydrogen. The luminous emission is subjected to ... action of the gas in which the discharge takes place, since the ... modifies to some extent both the distribution of the electric ... interposed between the electrodes and the temperature of the ...

T. H. P.

park Spectrum of Nickel under Moderate Pressures. FULHAM (*Phil. Trans.*, 1914, [*A*], **214**, 359—371).—The influence ... sure on the spark spectrum of nickel has been examined ... pressures up to eleven atmospheres. One of the most striking ... of the increase of pressure is the change in the character ... lines, which, according to the differences in behaviour, may ... divided into five groups. These groups contain, respectively, ... which show symmetrical reversion; (2) lines which reverse ... metrically; (3) lines which remain bright and sharp; ... which remain bright, but are symmetrically broadened; ... which are unsymmetrically broadened towards the red. ... general effect of an increase of pressure on the relative intensi-

ties of the lines is similar to that produced by the ......
self-induction in a spark circuit.

All nickel lines are displaced towards the red, the ....
being the same for lines of the first and second group ....
shifts are larger for unreversed lines, and are greater ...
which broaden unsymmetrically towards the red.

The observations point to the existence of two ....
λ 3514·14 and λ 3608·98, the wave-lengths of which are ...
identical with those of nickel arc lines.   B. W.

The Infra-Red Absorption Bands of Hæmoglobin
HARTRIDGE and A. V. HILL (*Proc. physiol. Soc.*, 1914, ...
Physiol., **48**).-- The absorption spectrum of reduced oxy- and car-
hæmoglobin was measured by means of a very sensitive ...
photometer. It was found that the absorption by reduced ....
greatest, by oxyhæmoglobin less, and by the carboxy- ....
still. The differences are sufficiently great for it to be ......
employ the method for determining the amount of .....
pounds present in a given solution.   W. I.

Simple and Complex Rotatory Dispersion   T. M.
LOWRY and T. W. DICKSON (*Trans. Faraday Soc.*, 1914, **10**, ...
Compare P., 1913, **29**, 185). All cases of rotatory ....
may be represented by Drude's formula. Simple dis-
persion may be expressed by the equation a ......
complex rotatory dispersion requires two or more terms ....
which may be negative. Anomalous dispersion is probably ...
many instances to dynamic isomerism.   C. H.

An Enclosed Cadmium Arc for Use with the Polari-
T. MARTIN LOWRY and H. H. ABRAM (*Trans. Faraday Soc.*,
10, 103—106).-- For substances with simple rotatory dispersion
preceding abstract), measurements with light of two wave-
such as the green and violet mercury lines, are sufficient to deter-
mine the form of the dispersion curve. For more complex dis-
cadmium arc may be used. The arc passes between solid
electrodes of solid cadmium in a vessel exhausted by a small
Gaede pump. When the vacuum is good, the arc will not
start itself, but usually the passage of a spark from an in-
is necessary   There is a silica bridge between the electrodes
the tube has two quartz windows.

a- and β-Methylglucoside show simple rotatory disper-
ratios for the violet and green mercury lines being the same
the green and red cadmium lines.   C. H.

The Constitution of Liquid Mixtures and Their Rotatory
Power.   A. COTTON (*Trans. Faraday Soc.*, 1914, **10**, 91—
The determination of the optical rotatory power and of the mag-
netic birefraction of the same mixture of liquids is proposed as a
means of determining whether complexes are present.   C. H.

Rotatory Power of Mixed Crystals, NaClO₃–AgClO₃ G. Pertcca (*Atti R. Accad. Sci. Torino*. 1914, **49**, 1127—1134. Compare Retgers, A., 1890, 1208; Foote, A., 1902, ii, 453).—The rotation of mixed crystals of sodium and silver chlorates varies not only among crystals from one and the same crystallisation, and from sector to sector of an individual crystal. The crystals show various optical anomalies, the double refraction of two kinds increasing with the content of silver chlorate. The specific gravities have been measured, and are found to be in accord with Rüdorff's additive law. Monometric silver chlorate has an approximately constant specific gravity of about 4·20 in mixed crystals of all compositions, and its specific rotation is 12·65°, this is about four times that of sodium chlorate.   T. H. P.

Optical Activity of Chemical Compounds without A. Werner (*Compt. rend.*, 1914, **159**, 426—429).—The author has prepared an optically active compound containing no but similar in composition to the cobalt triethylenediamine $[Co en_3]X_3$, en representing $NH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$. In place of molecule of ethylenediamine there is in the new compounds molecular complex $[(OH)_2Co(NH_3)_4]X$, their asymmetric constitution being represented by
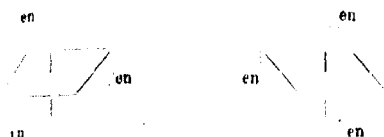
The salts prepared were the *bromides*, having the composition $[OH]_2Co(NH_3)_4]_3)Br_6,2H_2O$, the active forms being prepared by crystallisation from their r-bromocamphorsulphonates with sodium salt. The active *d*-salt prepared in this way crystallises in greyish-brown plates and is very soluble. It has $[\alpha]_{5461}$ varying from to 4500°, its rotatory power diminishing rapidly in aqueous solution, the salt becoming inactive after two hours.
                                                              W. G.

Existence of Racemic Tartaric Acid in Solution. latour (*Trans. Faraday Soc.*, 1914, **10**, 80—83. Compare A., 1913, 747).—When *d*- and *l*-tartaric acids are mixed in unequal portions in solution, the measured rotatory dispersions are those that would be expected if the two acids remained uncombined. Mixtures of *d*-tartaric acid and racemic acid also behave in solution as if the latter compound were dissociated into its components.
                                                              C. H. D.

Rotatory Power of Tartaric Acid. G. Bruhat (*Trans. Faraday Soc.*, 1914, **10**, 84—90).—The rotatory power of fused and cooled tartaric acid has been observed at temperatures from 180° downwards, and for light of different wave-lengths. The dispersion is normal at 180°, but becomes anomalous below 100°.

The dispersion curves are plotted together with those deter___
by Arndtsen (*Ann. Chim. Phys.*, 1858, [iii], **54**, 403) for ___
solutions of various concentrations, and exhibit a compar___
larity. The only hypothesis which will account for the ___
is that of the presence of two compounds of opposite ___
power, in proportions varying with the temperature and ___
centration, in both the solutions and the undercooled ___
of these compounds being ordinary tartaric acid, the other ___
be a complex aggregate.

Cryoscopic determinations in water by acetic acid show ___
quantity of the polymeride cannot much exceed 2 ___
have a rotatory power of from −80° to −200. The ___
parable with the rotatory power of solid rubidium tartrate.

C. H.

Discovery of the Sensitiveness of Silver Salts to L___
Icilio Guareschi (*Atti R. Accad. Sci. Torino*, 1914, **49**, 1083—___
The author regards Homberg's observation in 1694 (compare ___
this vol., ii. 234) as of little importance, since it refers ___
nitrate in contact with organic matter, which accelerates ___
composition of the silver salt, and since also it was known ___
earlier, before the time of Boyle (1663), that silver salts ___
in the light or in the air. Of far greater importance ___
development of photography were the investigations of S___
(1727), and particularly those of Beccari (1757) and Scheele ___
The invention of the dark chamber is due to G. B. Porta ___
1540—1615).

T. H.

Radium Constants on the International Standard.
Ernest Rutherford (*Phil. Mag.*, 1914, [vi], **28**, 320 ___
recalculation of the radioactive magnitudes in the ___
"Radioactive Substances and their Radiations" is given ___
basis of the International Standard. The equilibrium of ___
radium to uranium is now 3.23×10^{-7}, the yearly product ___
helium per gram of radium, calculated 163, found 164 ___
the total observed heating effect per gram of radium in ___
with its first four products is 134.7 calories per hour, made ___
radium, 25.1; emanation, 28.6; radium-A, 30.5; B and ___
the equilibrium volume of emanation per gram of radium ___
lated, 0.62, found 0.63 cu. mm.; number of a-particles ___
per second per gram of radium, itself, 3.57×10^{10}, ___
with first four products, 14.3×10^{10}; the total positive ___
the latter case, 33.2 *E.S.U.*, or 1.11×10^{-9} *E.M.U.* ___
negative charge carried by the β-particles of radium-B ___
18.3 *E.S.U.*; the total saturation current due to a-rays ___
of emanation, itself, 2.89×10^{6} *E.S.U.*, and with ___
9.94×10^{6}.

With regard to the heating effect of the emanation ___
lated from the kinetic energy of the a-particles expelled ___
is 7% lower than the observed, the following explanation ___
gested. The energy of the electronic distribution of an ___

expected to increase with increase of the nuclear charge, or the mass of the α-particle may be expected to be accompanied by increase of the energy of the electronic distribution, and the expulsion of the β-particle by the opposite effect. The relative heat effect of radium-B and C', as compared with that of the radium and radium-A, is less than the calculated, in agreement with this view, since β-rays as well as α-rays result in the change radium-B and C'. It is calculated that of the total heat effect of the α-ray changes, some 90% is due to the kinetic energy of α-particle expelled and 10% to loss of internal atomic energy in manner indicated.

From the value for $nE = 1.11 \times 10^{-9}$ E.M.U., where n is the number of α-particles per gram per sec. of radium itself, and E is the charge each particle carries, the half-period of radium on the international Standard is 1690 years. The experimental determinations give 2000 years (Boltwood), 1800 years (Keetman), 1730 (Stefan Meyer).

F. S.

Mass and Velocities of α-Particles from Radioactive substances. SIR E. RUTHERFORD and H. ROBINSON (*Phil. Mag.*, [vi], **28**, 552—572).—From the mean of recent determinations of atomic weight of helium, 3·998, and the value of e/m for the hydrogen atom, 9570, the value of e/m for the α-particle, or helium carrying two positive charges, should be 4826, whereas the best experimental value is 5070. To test as thoroughly as possible whether the value of e/m for a high speed positive particle agrees with the value from electrochemical data, experiments have been made, to an accuracy of 1%, on the value of e/m of the α-rays, by measuring the deflexions of a narrow pencil of α-rays taken by the photographic method, in very carefully determined electromagnetic and electrostatic fields. The final results for the value of e/m of the α-particles of radium emanation, radium-A and radium-C, lay between 4813 and 4826, the mean value being which agrees with the calculated result within the limits of

The initial value of the velocity of the α-particles of radium-C is 1.922×10^9 cm. per second, about 7% lower than the usually accepted value. On the new data, the development of heat calculated from the kinetic energy of the α-particles for radium and its products is 7% less than the observed, and part of that effect is probably due to other sources (see preceding abstract).

Special search was made for atoms differing from the α-particle in mass or charge, and the conclusion is drawn that if any exist their number is certainly less than 1 in 10,000 of the number of α-particles.

F. S.

Connexion between the β- and γ-Ray Spectra. SIR ERNEST RUTHERFORD (*Phil. Mag.*, 1914, [vi], **28**, 305–319).—Previous investigations on the β- and γ-rays are discussed from the point of view of the general problem of radiation, and tentative conclusions drawn. The results of Chadwick (this vol., ii, 408) show that even

the intense lines in the magnetic spectrum of radium-B repre[...] a small fraction only of the total β-rays emitted. F[...] seems that β-ray magnetic spectra are probably conta[...] a superimposed line spectrum. The continuous spectr[...] ascribed to the escaping β-particle suffering in its eje[...] the nucleus of the atom several collisions of the ordin[...] with the electrons in the outer electronic distribution of [...] In addition, it is supposed that certain well-defined regio[...] part of the atom are set into definite vibration, when[...] "characteristic" γ-radiations of the atom arise and one [...] groups of β-rays of definite speed are expelled, which giv[...] spectrum observed. The conclusion that characteristic [...] a line spectrum of β-rays must accompany one another [...] out by the evidence. Radium-E, which gives only a conti[...] β-ray spectrum, gives little or no γ-radiation.

To explain their absence in such particular cases, the conc[...] is drawn that the direction of expulsion of the β-particle fr[...] nucleus with regard to the structure of the atom must be [...] and be the same for all the atoms. Thus if this direction [...] lie through one of the vibrating regions of the atom before [...] lated, neither γ-radiation nor "line" β-radiation is emitted [...] same explanation covers the remarkable anomalies exhib[...] the types and relative intensities of γ-rays emitted by the va[...] radio-elements. In the bombardment of atoms by cathode ra[...] sufficient speed, however, the rays enter the atoms in all direct[...] and all types of characteristic X-rays have a chance [...] excited.

Accepting Planck's relation between the frequency and ener[...] of radiation and his values for the numerical constant and [...] electronic charge, the experimental evidence is reviewed fr[...] point of view differing from that before propounded. The pr[...] effect of the ejection of the β-particle from the nucleus [...] excitation of γ-rays at one vibrating region of frequency [...] the energy of these γ-rays suffers partial or complete conv[...] into energy of "line" β-radiation in the same region or in an[...] vibrating region of frequency v_2. The energy of the β-part[...] these cases will be either $ph v_1$ or $ph v_1 - qh v_2$, where p and q [...] integers and h is Planck's constant. On comparing the ene[...] the lines in the β-ray spectrum of radium-B and C with th[...] quency of the γ-rays, numerous close agreements are obs[...] which can hardly be accidental. Thus the unit of en[...] $0.4284 \times 10^{13} e$, which enters as an integral multiple in th[...] Nos. 1 to 29 (A., 1913, ii, 899) of the β-ray spectrum of rad[...] is, within the experimental error, one-third of 1.25×10^{13}[...] energy of one of the strong lines of the γ-ray spectrum of radi[...] reflected from rock-salt at an angle of $1°0'$, as deduced by Pl[...] relation. Of twelve strong lines of the β-ray spectrum, the en[...] of six are multiples of $1.285 \times 10^{13} e$, and thirteen (includin[...] of the first six) are multiples of another unit, 0.74×10^{13}[...] corresponds with the line reflected by rock-salt at $1°40'$[...] γ-ray spectrum of radium-B and C, and is believed to be [...]

one component belonging to each radio-element. The two lines not so included in the β-ray spectrum correspond with ten times a third unit, $1·75 \times 10^{15}$, which again corresponds with the γ-ray line of shortest wave-length yet observed, that reflected from rock-salt at an angle of $0°43'$. With regard to the β-ray spectrum of radium B, the evidence is similar, but less conclusive, on account of the large number of the γ-ray spectrum. Two of the strong lines are expressed as multiples of $0·870 \times 10^{15}$, to be expected of the γ-ray reflected at $1·24'$. But the γ-ray lines reflected at $10°$ and $9°$ not appear to be responsible for any of the β-rays.

Many some as yet untested deductions on the relation between spectra of β-rays excited by characteristic X rays and the length of the latter are drawn.   F. S.

Number of Ions Produced by the β- and γ Radiations of Radium H. G. J. MOSELEY and H. ROBINSON (*Phil. Mag.*, 1914, **28**, 327 337).—The total number, N, of pairs of ions produced in air by the γ-rays of radium B and C in equilibrium with a gram of radium is determined to be $1·22 \times 10^{15}$, whereas the α rays of radium produce $8·46 \times 10^{15}$. The ratio between these quantities is $6·94$, whereas the heating effects observed are $6·4$ and 1 per hour. In the following table the values of N, the calculated heating effect, and the average energy emitted, per atom, are given for the β and γ rays of radium B and C:

	$N/10^{15}$	Heating effect (cal. per hour).	Average energy per atom ($\times 10^{-6}$ erg.).
β rays of radium B	$0·325$	$1·71$	$0·55$
β rays of radium C	$0·64$	$3·35$	$1·09$
γ rays of radium B	$0·084$	$0·44$	$0·14$
γ rays of radium C	$1·134$	$5·96$	$1·91$
β and γ rays of radium B	$0·41$	$2·15$	$0·70$
β and γ rays of radium C	$1·774$	$9·3$	$3·02$

In Rutherford's original theory, the figures in the last two lines of the last column should be the energy of the β-particle which has passed without exciting γ-radiation. In the case of radium C, however, a few β-particles with energy as high as $3·9 \times 10^{-6}$ erg. have been observed. In the case of radium B the fastest β-ray gives as the energy $0·6 \times 10^{-6}$ erg.   F. S.

Secondary γ-Radiation D. C. H. FLORANCE (*Phil. Mag.*, 1914, **28**, 363 367. Compare this vol., ii, 160). Using equal masses and area of thin radiators, carbon, aluminium, copper, zinc, tin, least the amount of γ-radiation scattered by the radiator is the same after it has passed through $0·084$ cm. of lead. After passing through $0·202$ cm. of aluminium the lead radiator produced more scattered radiation than the others. This extra radiation from lead is probably a characteristic radiation. The scattering seems to be simply proportional to the number of electrons in atom or to the weight of the atom, an electron in a light

aluminium atom scattering to the same extent as one atom of lead. The loss of energy by the γ-ray to the increases with the angle of scattering, and the penetrating of the scattered radiation depends essentially on the scattering and not on the material of the radiator.

The Distribution of Energy in the Different Types of Rays Emitted from Certain Radioactive Substances. JADWIGA SZMIDT (*Phil. Mag.*, 1914, [vi], **28**, 527—5 determination of the total number of ions each type of ray duces in air or other gases gives the ratio of the energies different types if it is assumed that the same proportion of energy of different rays is spent in ionisation and that the required to produce an ion is the same for γ-rays of different penetrating power. To test the second point, the total ionisation in various gases by γ-rays of different hardness was determined. For the soft γ-rays of radium-*D* the ionisation produced in dioxide, carbon dioxide, and air is proportional to the in these gases, but in the case of hydrogen sulphide greater tion is produced, as is the case also with *X*-rays. In the the hard γ-rays from radium-*B* and radium-*C*, the ionisation proportional to the absorption.

Of the total γ-ray energy of radium-*D*, the hard γ-rays between 17 and 35%. In the γ-rays of radium-*B* and energies of the soft rays of radium-*B*, the hard rays of radium and the rays of radium-*C* are estimated as in the ratio 1 : 45 : 639.

Ordinals or Atomic Numbers? A. VAN DEN BROEK (*Phil. Mag.*, 1914, [vi], **28**, 630—632).—The author criticises Rydberg's suggestion (this vol., ii, 599) that the frequencies of the *X*-rays are related to the "ordinals" which are two units higher than atomic numbers. The hypothesis that the frequencies are equal to the atomic numbers affords a more satisfactory account of experimental results, and also affords a basis for the explanation of observations on the scattering of α-particles and of Röntgen.
H. M.

The Absorption Coefficients of *X*-Rays. W. H. BRAGG S. E. PEIRCE (*Phil. Mag.*, 1914, [vi], **28**, 626—630).—The method of determining the wave-lengths of *X*-rays by reflexion from crystal surfaces has made it possible to determine the relation between wave-length and absorption coefficient. The waves examined are those emitted by anti-cathodes of silver, palladium and rhodium, each of which yields a spectrum consisting of two well-defined intense lines. Each wave-length was measured by reflection from a rock-salt crystal, and its absorption coefficient in various metals determined. Barkla's rule that the ratio of absorption coefficients is independent of the wave-length of the rays is confirmed over a wide range.

The results suggest that the absorption coefficient of any

of atomic number N is equal to CN^4, where C has constant over prescribed ranges. The constant changes its value in passing through the wave-lengths of the Rh–Pd–Ag examined. According to Darwin, the absorption coefficient as the 5 2 power of the wave-length of the rays absorbed, this, combined with the preceding, gives the very general rule the atomic absorption coefficient, defined as the proportion of energy of the X-ray pencil which is absorbed on crossing a which lies one atom to every square centimetre, is where λ is wave-length of the X-ray, C is equal to for all values of N between 13 (Al) and 46 (Pd), and to for all greater values.   F. S.

Effect of X-Rays on the Action of Certain Enzymes. A. HANS (*Amer. J. Physiol.*, 1914, **35**, 224—238).—The author experiments which indicate that a short exposure of diastase, and other enzymes to X-rays increases the activity, the exposure be prolonged for more than five minutes the to diminish the activity of the enzyme. Between these extremes there lies a point at which the radiation is ineffective, accelerating and the inhibiting effects are slight, but seem to definite.   H. W. B.

Experiments on the Active Deposit of Radium. E. M. WELLISCH (*Phil. Mag.*, 1914, [vi], **28**, 417; *Amer. J. Sci.*, 1914, [iv], 283-304. Compare A., 1913, ii, 905). In a series of experiments on the distribution of the active deposit from radium emanation in ethyl ether, it was found that neither a positive nor negative agent exerts any appreciable effect, the proportion reaching the central electrode of a cylindrical vessel being 10%. Hence the parts of active deposit at the end of their recoil paths in ether uncharged, the amount reaching the electrodes arriving there diffusion.

When the emanation in relatively large quantity is mixed with air the active deposit particles in the gas form large aggregates which acquire positive and negative charges from the ions present the gas. The formation of these aggregates appears to cease rapidly when the concentration of the emanation and the degree ionisation it produces sink below a certain value. Under these conditions, the particles in the gas are practically all neutral, and reach the electrodes through simple diffusion, the diffusion coefficient in dry air at atmospheric pressure and about 20° being approximately 0·045 cm.^{2} sec.$^{-1}$.   F. S.

The Distribution of the Active Deposit of Radium in Electric Fields. H. P. WALMSLEY (*Phil. Mag.*, 1914, [vi], **28**, 751. Compare A., 1913, ii, 905).—In the case of the radium active deposit, some 5 to 10% is deposited on the anode, and this been further investigated. This part is ascribed to the recoil of unchanged particles of radium-A, and no negatively charged particles exist.   F. S.

Origin of the Electron Emission from Glowing Solids.
FRANK HORTON (*Phil. Trans.*, 1914, [A], **214**, 277—294). — Experiments
on the electron emission from Nernst filaments have been made
with the object of throwing further light on the origin of the
emissive effect and of testing the "chemical action" theory of the
working of an oxide electrode. A comparison was made of the
electron emission from a filament (1) when heated by a direct
and by alternating currents; (2) when heated by the same direct
current and heated without conducting the heating current;
(3) heated in the ordinary manner and compared with the effect
of the same material when heated on platinum. These experi-
ments indicate that the electron emission is not connected either
directly or indirectly with the electrolysis which accompanies the
passage of the current. At a given temperature, the emission is
the same whether the current through the filament is large or
small. From this it may be inferred that the action of a Wehnelt
cathode is not due to the recombination of electrolytically produced
calcium and oxygen, as has been suggested.

No definite conclusion can be drawn from the results as
to whether the electron emission is purely a thermal effect or is
due in some way to chemical action. The fact that the emission
increases when a chemically active gas is allowed into the dis-
charge tube may or may not be due to chemical action. It is
probable that the cause of the increased activity is not the same in
different cases.   H. M. D.

Radium : Uranium Ratio in Carnotites. S. C. LIND and
C. F. WHITTEMORE (*J. Amer. Chem. Soc.*, 1914, **36**, 2066—2082).—
The samples of carnotite used in this investigation were representa-
tive of the principal occurrences in Colorado and Utah, those
containing from 1·5% to 33% of U_3O_8 were included. Samples
representing large quantities of ore (from a few hundred to
several tons) gave a ratio Ra : U identical with that from pitch-
blende, $3·33 \times 10^{-7}$. Samples from small quantities of ore
exhibited abnormal ratios, ranging from $2·48 \times 10^{-7}$ upwards.
These abnormal ratios are probably due to a transport of
radium within a bed of ore, producing local differences which are
neutralised when large quantities of ore are mixed.

Carnotite has a high emanating power, varying from bed to bed.
In order to obtain concordant results by Boltwood's emanation
method, it was found desirable to make the determination of the
emanating power and the emanation liberated by solution of the ore
complementary to each other by determining the emanation liber-
ated by solution on the same sample from which the emanating
power had just been determined. Radium can be accurately
determined by the emanation method in one operation, either in
solution or by ignition from tubes in which it has been sealed for a
month to attain equilibrium.   E. G.

**The Electrical Resistance and Critical Ranges of Pure
Iron.** G. K. BURGESS and I. N. KELLBERG (*J. Washington Acad.*,
1914, **4**, 436—440). —The variation of the resistance of pure

...temperature has been examined between 0° and 950°. The method employed consisted in comparing the resistances of iron and platinum wires, which were wound on the same support and placed in an exhausted quartz tube heated in an electric furnace. With the aid of a drum-chronograph, the times at which the resistances were measured could be accurately recorded, the resistance of the platinum wire affording a measure of the temperature of the iron wire at any moment.

The results show that the resistance of iron increases at a gradually increasing rate until the neighbourhood of the first critical region (A_1) is reached. This region is characterised by a point of inflexion on the resistance temperature curve at 757°. As the temperature is further increased, there is an abrupt fall in the resistance at about 894°, and the reverse change occurs at approximately the same temperature when the temperature is allowed to [fall]. This second critical region (A_3) extends over an interval of [temp.]. Whilst the change A_2 is reversible and does not appear to be associated with any alteration in crystalline structure, the change seems to be progressive and (thermo-electrically) non-reversible, and furthermore it is associated with a change in crystalline form.

H. M. D.

Measurement of Oxidation Potentials at Mercury Electrodes. I. The Stannic-Stannous Potential. GEORGE SHANNON FORBES and EDWARD PAYSON BARTLETT (*J. Amer. Chem. Soc.*, 1914, **36**, 2030—2040).—The work of earlier observers on the stannic-stannous potential has not given concordant results, and the present investigation has therefore been carried out.

It has been found that mercury is superior to platinum for use in measuring oxidation potentials of low intensity as results are obtained more rapidly and are less liable to be vitiated by irregularities in surface energy of the electrode or by the presence of traces of oxygen.

The potentials of mixtures of stannic and stannous chlorides containing $\frac{1}{4}$ gram-atom of tin per litre in hydrochloric acid of three different concentrations have been measured at mercury electrodes at 25°. Some measurements were also made of mixtures containing only $\frac{1}{8}$ gram-atom of tin per litre. The potential has been found to be nearly independent of the concentration, but is very slightly more electro-negative in the more dilute solutions.

In order to ascertain the values which should be observed if acid could be eliminated without the appearance of hydrolysis, the potentials for selected values of the concentration ratio have been plotted against the several concentrations of acid employed and extrapolated to zero concentration of acid; the graphs thus obtained are nearly straight lines. Up to two gram-mols. of hydrochloric acid per litre the potentials are expressed accurately by the formula $= 0.426 + 0.030 \log Sn^{IV}/Sn^{II} - 0.011 \times$ concentration of hydrochloric acid, provided that sufficient acid is added to prevent hydro...

E. G.

Diffusion and Membrane Potentials. E. B. R. Pu...
(Trans. Faraday Soc., 1914, **10,** 160—166).—The membrane p...
has been determined when two solutions of sodium betw...
different concentrations, are separated by parchment. C...
electrodes are used. The potentials observed are conside...
than the ordinary diffusion potentials. The effect appears...
decrease the mobility of the anion as compared with that...
cation, but the membrane is never completely imperme...
anion.   C. H...

Studies on a New Kind of E.M.F. I. REINHARD BE...
(J. Amer. Chem. Soc., 1914, **36,** 2040—2045).—The *E.M.F...*
galvanic cells composed of insoluble inorganic liquids and aqu...
solutions (A., 1913, ii, 469) is discussed, and it is shown that...
change of the *E.M.F.* of such systems must be due to the...
of potential difference located at the junction of the organic...
and the aqueous solution. The observations on cells conta...
salicylaldehyde as a middle conductor afford an imitation...
electrode-like potential differences between certain living...
and aqueous solutions (Loeb and Beutner, A., 1912, ii, 66...
shown that the potential difference at the junction of the...
phases does not depend on ionic mobility as does the pote...
difference between miscible solutions, but must have...
characteristic of potentials at metallic electrodes.   E...

Studies on a New Kind of E.M.F. II. Cell Arrangement
of Aqueous and Nitrobenzene Solutions Containing On
Common Ion in Both Phases. REINHARD BEUTNER *(J. Am*
Chem. Soc., 1914, **36,** 2045—2059).—In the preceding paper, referen
has been made to the existence of interphase potential differen
with properties resembling electrode potentials.

The *E.M.F.* of cells consisting of aqueous and nitrobenzene sol
tions has now been measured. The solutions in contact with each
other always contain one common ion, and the potential differen
at the nitrobenzene water interphase can therefore be easily calc
lated from the thermodynamic formula. It is proved that the to
E.M.F. of cells which consist of two nitrobenzene solutions i
contact with each other between two identical aqueous solutions
located at the phase junctions, and not at the junction of the tw
nitrobenzene solutions.

Ostwald has suggested that a selective ionic permeability of
membranes is the cause of physiological currents. According to th
hypothesis, the *E.M.F.* produced by a water-immiscible layer is n
located at the phase-junction but inside the layer or membra
This theory does not accord with the experimental results obtain
in the present investigation.   E. G

Passivity of Metals. HORACE G. BYERS and SETH C. LANG
(J. Amer. Chem. Soc., 1914, **36,** 2004—2011).—It has been shown i
earlier work (Byers, A., 1908, ii, 1026; Byers and Darrin, A., 19
ii, 579; Byers and Morgan, A., 1911, ii, 1057; Byers and Lang

1913, ii, 552) that the establishment of the passive state in iron as an anode is affected by the character and condition of the electrolyte, the temperature, the current density, the rate of passage of the current, and the character of movement of electrolyte. Experiments are now described which indicate another factor must be added to these, namely, the concentration of the dissolved oxygen about the anode, and that this is apparently the determining factor. When all these factors are taken into account, constant results can be obtained with respect to the time required to render iron passive with a given current in nitric acid, and a critical current density in nitric acid can be obtained.

Passivity, when not caused by a visible film of oxygen, is considered to be due to the fact that the rate of ionisation of certain metals is not sufficient to carry a current of more than a certain value. When such current density is exceeded, oxygen electrodes, consisting of occluded oxygen, are formed in electrolytes consisting of oxygen compounds. Non-anodic passivity is also regarded as due to inclusion of oxygen and consequent protection of the metal from attack.

E. G.

Electro-deposition of Cadmium. I. and II. FRANK C. MATHERS from M. MARBLE (*Trans. Amer. Electrochem. Soc.*, 1914, **25**, 315, 319–333).—I. A review of the work done in the refining and commercial plating of cadmium. Reference is made to work done with (1) sulphate solutions, (2) nitrate solutions, (3) haloid solutions, (4) silicofluoride solutions, (5) cyanide solutions, (6) phosphate solutions, (7) ammoniacal solutions, (8) oxalate solutions, acetate, formate, lactate, and succinate solutions, and (10) tartrate solutions.

II. A large number of experiments have been carried out with the object of determining which salts of cadmium are best suited for giving smooth, adherent, and non-crystalline deposits. Baths were made up of various cadmium salts containing 4% of cadmium, and electrolysed between cadmium electrodes with a cathode current density of 0·4 amp. per 100 sq. cm.; the solutions were stirred at intervals. The deposits obtained from ammoniacal and alkaline citrate baths were hopelessly spongy. The deposits from solutions of acetate, bromide, iodide, sulphate, phosphate, and chloride were rough and crystalline. A number of experiments are described with these baths to which various other substances had been added, for example, a bath containing 4% of cadmium as chloride, 10% of sodium chloride, 5% of hydrochloric acid, and 0·1% of peptone gave a fairly smooth, finely crystalline deposit. A bath of the same composition as the foregoing with the addition of 10% of ferric chloride gave a much better deposit. Manganese, aluminium, or calcium chlorides did not improve the deposit in the same way as iron did. The deposits obtained with solutions of bromide and iodide were crystalline and rough. Solutions of fluoride, silicofluoride, borofluoride, and perchlorate containing 4% of cadmium, 0·5—5·0% of the free acid and 0·2 gram of peptone, glue, or

phloridzin or 4 drops of oil of cloves gave excellent deposits several times in these cases spongy places, rough projections, and spots were formed, but these are attributed to the presence of particles of anode slimes, since they were not formed when the anode was amalgamated. It is shown that the same substances, oil of cloves, glue, peptone, and phloridzin, which have been previously shown to give quite good deposits in the case of lead, also produced good deposits in the case of cadmium, although it was generally much more difficult to obtain good deposits with cadmium than with lead.   J. F.

A Thermo-regulator for Thermostats at Temperatures Very Close to Room Temperature. CHARLES W. R. Power (*J. Soc. Chem. Ind.*, 1914, 33, 899—900).—A regulator is described for use with thermostats at temperatures either a few degrees below or above atmospheric temperature. The regulator consists of the usual toluene filled vessel, which is fitted at the top with two side tubes at different levels; the top one leads into the thermostat and the lower one into the sink, and both serve to conduct a stream of ice-cold water. The top of the regulator is closed by a cork, which carries a glass tube, by means of which ice-cold water enters the regulator, and a copper wire which terminates at the upper end of the capillary of the regulator. A second wire is fused into the regulator in such a position that it is always in contact with the mercury column. These two wires are connected through an accumulator with a small electro-magnet. The magnet when active operates a lever which deflects the flow of ice-cold water from the sink into the thermostat, and at the same time breaks the circuit of the electrical heater, so that the temperature is regulated very quickly. Using such an instrument, the author was able to maintain a temperature of 27° within ±0·5° in a 3-litre thermostat with the atmospheric temperature at 30°.   J. F.

Capacity for Heat of Metals at Low Temperatures. E. H. GRIFFITHS and EZER GRIFFITHS (*Phil. Trans.*, 1914, [*A*], 214, 319—357). —The specific heats of a large number of substances have been measured at the ordinary temperature, and also at liquid air and liquid hydrogen temperatures, but there have been as yet no direct measurements of the true specific heats at intermediate temperatures. In order to bridge the gap, the authors have worked a method for maintaining the temperature of an enclosure constant at any point between that of the room and −165° by a direct application of the Joule-Thomson effect. The method employed in the measurement of the specific heats of metals depends on the determination of the rise in temperature of a block of the metal which is suspended in the constant temperature enclosure and supplied with a measured quantity of electrical energy.

Experiments were made at various temperatures within the above-mentioned range on aluminium, copper, zinc, silver, cadmium, lead, iron, and sodium. Atomic heat temperature curves have been constructed from these data in combination with the results obtained by Nernst at liquid air and hydrogen temperatures

By comparing the experimental curves with the requirements of the formulæ put forward by Einstein (*Ann. Physik*, 1907, [iv], **22**, Nernst and Lindemann (A., 1911, ii, 466), and by Debye (1912, ii, 1134), it is found that none of these formulæ is capable of representing the results over the entire temperature range. Debye's formula appears to give the nearest approximation for the lowest portion of the range, but systematic divergences occur at the higher temperatures. This may be due either to the assumptions made by Debye being valid only at very low temperatures, or it may mean that heat energy, additional to that involved in the three degrees of freedom ascribed to the atom, must be taken into account. Above liquid air temperatures the three formulæ are capable of representing the results approximately, but in some cases the discrepancies are considerable.

H. M. D.

Metastability of the Metals in Consequence of Allotropy and its Significance for Chemistry, Physics and Technics. ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 905. Compare this vol., ii, 202).—A review of the earlier literature dealing with the specific heat of the metals affords evidence that the specific heat depends in many cases on the previous history of the metals. For copper, zinc, lead, aluminium, etc., the specific heat temperature curve is not continuous, but changes abruptly at one or more points. This behaviour is in agreement with the dilatometric observations, which indicate the existence of proper modifications of some of these metals.   H. M. D.

Determination of the Freezing Point for Salt Solutions. H. VAN DER LAAN (*Chem. Weekblad*, 1914, **11**, 925—927).—In determining the freezing point of a salt solution, homogeneity of the liquid must be ensured by vigorous agitation. Failure to observe this precaution leads to inaccurate readings for such solutions, but is immaterial for such liquids as water or milk.   A. J. W.

Boiling Points in Homologous Series. S. SUGDEN (*Chem. Soc.*, 1914, **110**, 152—153, 165—168).—It is found that the boiling points of the members of homologous series of carbon compounds can be satisfactorily represented by means of the formula $M \cdot b = \sqrt{M} + a M / b$, in which M is the molecular weight, b the boiling point, and a and b are constants. The formula is shown to be applicable to the paraffins, alkyl haloids, aldehydes, ketones, acids, amines, alkyl cyanides, normal primary and secondary alcohols, hydrosulphides, esters, nitroparaffins, ethers, olefines, and aromatic hydrocarbons. The average difference between the observed and calculated boiling points for some one hundred and fifty-one compounds is 1·63°. The values of a vary to a comparatively small extent from one series to another, the aromatic hydrocarbons having the highest value (45·71) and the olefines the lowest (41·9). The values of b vary to a much larger extent, the extremes being shown by the alkyl iodides ($-2038·0$) and the nitroparaffins (+591).

H. M. D.

Vapour Pressures of Silver, Gold, and Bismuth Amal... ERMON DWIGHT EASTMAN and JOEL H. HILDEBRAND (J. Amer. ... Soc., 1914, 36, 2020—2030).—In continuation of a study of ... of concentrated solutions from the point of view of ... tions (Hildebrand, A., 1913, ii, 755), measurements ... made of the vapour pressures of silver, gold, and bismuth ... at about 318° by the method used in the case of the ... (loc. cit.).

As silver is but sparingly soluble in mercury at 318°, ... determination was made, namely, with an amalgam ... 1·27% of silver. In this case Raoult's law was obeyed ... limits of experimental error.

Measurements with gold amalgams, at concentrations ... 23·7% of gold, showed the separation of a solid phase at ... 16·5% concentration. In the more dilute amalgams the ... pressures were greater than those calculated from Raoult's law.

Bismuth amalgams of all concentrations are liquid at ... also give higher vapour pressures than those calculated by Raoult's law.

For the gold and bismuth amalgams, equations, ... derived by Laar (A., 1910, ii, 583; 1913, ii, 670), are ... satisfactorily express the values observed.   E. ...

Method of Finding the Partial from the Total Vapour Pressures of Binary Mixtures, and a Theory of Fractional Distillation. M. A. ROSANOFF, C. W. BACON, and JOHN F. SCHULZE (J. Amer. Chem. Soc., 1914, 36, 1993—2004).—Rosa... Bacon, and White (this vol., ii, 766) have described a simple ... of measuring the partial vapour pressures of liquid binary ... which consists in distilling the mixtures and analysing ... secutive fractions. In some cases the analysis cannot be ... accomplished, and the experimental determination of the ... pressures would therefore be untrustworthy.

It is now shown that the partial pressures can be calculated ... the total vapour pressure by means of the general relation:

$d\pi/dr = [(P_1 - P_2)/(\log P_1 - \log P_2)] \log [p_1(1 - ...$

where r is the molar fraction of one of the components in liquid, π the total pressure, p_1 and p_2 the partial pressures, ... and P_2 the vapour pressures of the isolated compounds. Cal... tions have been made by means of this expression for mixtures carbon tetrachloride and benzene, ethyl iodide and ethyl chloroform and acetone, and benzene and toluene, and the res... agree satisfactorily with those obtained experimentally.

A theory of fractional distillation is presented for the case which the vapour escapes from the still without having under... any reflux condensation. This theory is based solely on the principles involved in the equation given in the preceding paragraph.   E. ...

Measurements of Isotherms of Hydrogen at 20° and 15 PH. KOHNSTAMM and K. W. WALSTRA (Proc. K. Akad. Wet. Amsterdam, 1914, 17, 203—216).—The authors have investi...

compressibility of hydrogen at 15·5° and 20° for pressures ... from about 200 to about 2300 atmospheres. The lower ...erature was chosen in order to enable a comparison to be made ... results with those obtained by Amagat.

... preliminary experiments with air, it was found that at high ...res the mercury quickly became contaminated, in consequence ... formation of mercuric oxide. This prevented the carrying ... measurements on the pressure-volume relations of air and ...

H. M. D.

Hydrogen Isotherms of 20° and 15·5° between 1 and ...0 Atmospheres. K. W. WALSTRA (*Proc. K. Akad. Wetensch. ...dam*, 1914, **17**, 217–224. Compare preceding abstract). The ...therms at 20° have been compared with those of Schalkwyk, ...hose at 15·5° with the data given by Amagat. For this pur-...sal equation of the form $PV = a + bD + cD^2 + dD^4 + eD^6$, in ... *D* is the density and *a*, *b*, *c*, *d*, *e* are coefficients. In so far ...comparison is possible, the author's observations appear to be ...sfactory agreement with Schalkwyk's. Between 700 and ... atmospheres, the values of *PV* given by the author's results ...mewhat greater than those calculated from Amagat's data, ...e difference is particularly marked for pressures above 2000 ...pheres.

H. M. D.

...thermals of Monatomic Substances and their Binary ...ures XVI. New Determination of the Vapour ...ures of Solid Argon down to −205°. C. A. CROMMELIN ...*K. Akad. Wetensch. Amsterdam*, 1914, **17**, 275–277. Compare ... ...81)—The vapour pressures of solid argon have been ...sured over the temperature interval −189·64° to −205·32°. ...pressures corresponding with these limiting temperatures are ...tively 49·78 and 3·830 cm. of mercury. The experimental ...ults are compared with the values calculated according to ...mulæ of Rankine and Bose, Nernst and Sackur. Sackur's ... which is based on Nernst's heat theorem, affords satisfac-...agreement at the higher temperatures, but there are wide ...ces at the lower.

... heat of sublimation of solid argon, calculated from the ...erature variation of the vapour pressure, falls from 47·36 at ...84° to 44·51 at −205·32°.

H. M. D.

New Relation between the Critical Quantities and the ...y of All Substances in their Thermic Behaviour. J. J.
...AR (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 451–465. ...are this vol., ii, 341).—A theoretical paper in which the author ...s at the conclusion that the quantity *a* in the van der Waals'
...tion is independent of the density over a very large range. ...molecular attraction in both the gaseous and liquid states is ...efore satisfactorily represented by a/v^2. Whether *a* is also ...pendent of the temperature cannot as yet be determined with

... XVI. ii.

perfect certainty. With reference to the quantity b ....
tion, the evidence is distinctly in favour of its depe.......
density and temperature. The significance to be attach.....
that of the volume (m) occupied by the molecules, and ....
assumption that $b = 4m$ must be discarded.

The thermal behaviour of a substance is not only depend....
the quantities a and b, which determine the critical ....
but also on the absolute value of the temperature at w....
substance is considered. Every substance passes from the ....
type to the ideal type when the temperature falls ceases
and approximates to absolute zero.   H. M.

Free Energy of Oxygen, Hydrogen, and the Oxi-
Hydrogen. GILBERT N. LEWIS and MERLE RANDALL (*J. Amer.*
Soc., 1914, **36**, 1969—1993).—In an earlier paper (Lewis, A.
ii, 112) an account was given of the general methods used
energy calculations. These methods have now been applied
determination of the free energy of oxygen, hydrogen, ...
hydrogen oxides. The calculations have been made from
existing data, but in some cases data have been employed
were obtained in the course of investigations not yet pub...

The following are the values (in calories) of the free e...
formation (F° 298) from the elements in their standard ...
ozone (O_3), 32,400; hydrogen (H), 30·550; hydrogen ion n
hydroxyl ion (OH′), −37·385; water (liquid), 56·6
(gas), −54,567; water (solid), −56,478; hydrogen per...
aqueous solution), −30,970; hydroperoxide ion (HO)...
hydrogen peroxide (liquid), −27,770; hydrogen per...
−24,270.   :

Combustion Calorimetry and the Heats of Combus-
Sucrose, Benzoic Acid, and Naphthalene. HOBART C. ...
(*J. Washington Acad. Sci.*, 1914, **4**, 434—435). A critical ....
the stirred water calorimeter, as used for bomb combust
been made, and it has been found that the chief source
may be avoided by the use of a suitably designed calor...
with resistance thermometers. Determinations of the heat
bustion of naphthalene gave 9622 ± 2 cal. per gram, with a
mum deviation from the mean of about 5 in 10,000 for ...
observations on the same sample. The value obtained for
acid was 6329 ± 1 cal. per gram, with a maximum deviation
5 in 10,000, and for sucrose 3949 ± 2 cal. per gram, with a
mum deviation of about 1 in 1000.

The results indicate that benzoic acid is the most suit...
three substances for calibration purposes. The vola...
naphthalene necessitates special precautions when this sub
employed, and sucrose is less well adapted, not only on ...
of the lower precision of the results, but also because of its
heat of combustion and its frequent failure to ignite.   H. M.

Flames with Ether. ALAN LEIGHTON (*J. Physical Chem.*, 18, 619—629).—Perkin (T., 1882, 41, 363) showed that when was evaporated in a shallow dish on a hot sand bath, a pale flame was produced, only visible in the dark, which did not the ether. This phenomenon had been previously observed by Döbereiner, and others. The author has investigated this and shows that it may be produced in many ways, among may be noted the following. A copper ball is heated to redness, and then allowed to cool until it just becomes in it is then suspended over a dish containing layers of filter soaked in ether, when a tall, blue flame is produced. The is produced at temperatures below dull redness, but above It has a comparatively low temperature, and the fingers be placed in it with impunity. It is shown that the flame is and when ether vapour is mixed with a small amount of and no hot surface is necessary. It may therefore be pro by mixing ether with a non-inflammable volatile liquid and the mixture to evaporate and lighting the mixture with or by mixing ether vapour with a non inflammable gas, carbon dioxide. Similar flames can be obtained by re ether by carbon disulphide; all the flames have low That from carbon disulphide and carbon tetra has a temperature of 90°.   J. F. S.

ory of Molecular Volumes. IV. GERVAISE LE BAS (*Phil.*, [vi]. 28. 439—466. (Compare this vol., ii, 173, 340, 539) influence of ring structure on the molecular volume has amined by reference to the data for a large number of containing one or more rings. The data in question the most part to homocyclic compounds, but heterocyclic are also considered.

relationships exhibited lead to the conclusion that molecular influenced by ring structure to an extent which depends number of rings and on the number of groups in the rings. in general is a contraction, which is contributed to by elements of the nucleus, and often by the atoms which are with these. The contraction is the same whether two rings are separated or condensed; from this it would seem common atoms of the two or three rings must have extra small volumes.

actions characteristic of the various polymethylene given as: *cyclo*propane, - 5·3; *cyclo*butane, 8·6; *cyclo* -12·3; *cyclo*hexane, -16·1; *cyclo*heptane, -20·16; *cyclo*octane, -24·0. The corresponding value for the benzene ring 7.

traction attributed to the influence of atoms or groups in ation with the elements of the ring nucleus is supposed characteristic of atoms or groups which possess residual this residual affinity is neutralised, the contraction, as appears. The following values are given for the contrac due to the different groups in combination with the

C_6H_5 nucleus: OH, -1.5; CN, -1.6; CH_2Cl, -1.9, $P_{...}$ NO$_2$, -2.7; COCl, -1.8; NH$_2$, -4.4; CO$_2$H, -2.8 ... particular effect is described as the volume anomaly.   H M

The Unit-Stere Theory of Molecular Volume. EASTER-
STONE (*Phil. Mag.*, 1914, [vi], 28, 600—606).—A ... unit-stere theory advanced by Le Bas (A., 1907, ... ratio V/W, where V is the molecular volume and W ... the valencies, may be considered as the product of the volume v and M/W, where M is the molecular w... member of a homologous series of compounds, M/W ... quantity $(a + n \cdot 14)/(a' + n \cdot 6)$, where a represents ... weight of the first member of the series, n the ... groups, and a' the sum of the valencies for the first ... the higher members of such a series M/W becomes ... stant and equal to 14/6 or 2·33. Since v also ten... stancy, the observed constancy of V/W in the higher ... homologous series can be readily explained. In so far ... members of such series are concerned, the observed var... V/W can be explained by the relative variations in th... v and M/W.   H M

The Unit-Stere Theory. GERVAISE LE BAS (*Phil. Mag.*, [vi], 28, 607—608).—A reply to Vanstone's criticism ... preceding abstract) The author considers that the ... volume is not divisible into factors represented by the volume and the ratio of the molecular weight to the sum valencies.   H M

Existence of Compounds in Binary Liquid M... J. HOWARD MATHEWS and RAYMOND D. COOKE (*J. Phys...*, 1914, 18, 559—585).—Starting from the expression ... Batschinski (A., 1913, ii, 928), the authors show that the specific volume curves of non-associated liquids are straight whereas those of associated liquids are concave toward the axis. The authors show that further evidence of the exist compounds in certain liquid mixtures is obtained by p... fluidity–specific volume isotherms of binary mixtures, and that this evidence supports the view that a maximum viscosity composition curve of a binary mixture is ... the presence of a compound. Twenty-four pairs of ... plotted in this manner, and of these nine exhibit max... the other fifteen give straight lines. The values used in ... are taken from the work of Dunstan (T., 1901, 85 ... and Rodger (T., 1897, 71, 360), Linebarger, Faust... New determinations have been made of the pairs acetic ... (56—44%), methyl alcohol–water (36—64%), propyl al... (50—50%), water–acetic acid (22—78%), water–pyridine ... acetic acid–pyridine (77—23%), ethyl alcohol–water ... chloral–water (88—12%), and chloral–ethyl alcohol (43—... The measurements were made at temperatures from $0°$ ...

full bibliography of the work done on viscosity, as far as it
to the chemical and molecular constitution and on the
properties of completely miscible liquids, is appended to the paper.

J. F. S.

Temperature-coefficients of the Free Surface Energy of
Liquids at Temperatures from −80° to 1650°. I. Methods
and Apparatus. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*,
1914, 17, 329−365).—An arrangement of apparatus is described by
means of which it has been found possible to make accurate
measurements of the surface tension of liquids at temperatures
between −80° and 1650°. A capillary tube, provided with a
sharp knife-edge opening, is immersed in the liquid perpendicular
to its surface, and a small bubble of gas is allowed to form slowly
at the end of the capillary tube. The pressure in the gas bubble
at the moment when the bubble is about to burst affords a measure
of the surface tension of the liquid. Provided that abnormally
great viscosities are not encountered, the author considers that the
results obtained with his apparatus are as accurate at 1650° as at
ordinary temperature.

The results obtained at different temperatures for a number of
organic substances and for several inorganic salts are recorded in
full. A comparison was also made between the surface tensions
of pure water and colloidal solutions of ferric hydroxide and silicic
acid. The curves showing the relation between the surface-energy
and the temperature are of the same kind, but those for the
colloidal solutions are situated above the curve for water.

H. M. D.

Temperature-coefficients of the Free Surface Energy
of Liquids at Temperatures from −80° to 1650°. II.
Measurements of Some Aliphatic Derivatives. F. M. JAEGER
and J. SMIT (*Proc. K. Akad. Wetensch. Amsterdam*, 1914,
17, 366−385).—Measurements of the temperature variation of the
free surface energy (μ) have been made for n-propyl alcohol,
ethyl alcohol, diethyl ether, ethyl formate, ethyl chloro-formate,
ethyl acetate, methyl *iso*butyrate, ethyl *iso*butyrate, *iso*butyl *iso*-
butyrate, acetone, methyl propyl ketone, ethyl acetoacetate, methyl
and ethyl acetoacetate, ethyl propylacetoacetate, methyl, ethyl,
propyl, *iso*butyl and amyl cyanoacetates, chloroform, carbon
tetrachloride, and *iso*butyl bromide. In most cases dμ/dt decreases
with rise of temperature. Where an increase was observed this
was traced to decomposition of the substance. H. M. D.

Temperature-coefficients of the Free Surface Energy of
Liquids at Temperatures from −80° to 1650°. III. Measure-
ments of some Aromatic Derivatives. F. M. JAEGER and M. J.
SMIT (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, 17, 386—394).
The following substances were examined : nitrobenzene, o-nitro-
aniline, dimethylaniline, o-toluidine, thymol, methyl,
and benzyl benzoates, salicylaldehyde, acetophenone, and

a-campholenic acid. The curves obtained by plotting the molecular surface energy against the temperature are concave to the axis the case of nitrobenzene, o-nitrotoluene, aniline, and o-toluidine indicating that $d\mu/dt$ increases with the temperature. In their behaviour these substances resemble water, but differ from the majority of the substances examined in the previous paper (preceding abstract).
                                                                H. M.

Temperature-coefficients of the Free Surface Energy of Liquids at Temperatures from −80° to 1650°. IV. Measurements of Some Aliphatic and Aromatic Esters. F. M. JAEGER and JUL. KAHN (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 395—405).—The data recorded refer to amyl acetate, ethyl and ethyl malonate, ethyl bromomalonate, ethyl benzylethyltate, methyl and ethyl tartrates, methyl, ethyl and phenyl succinate, methyl cinnamate, and o-nitroanisole. The surface-energy-temperature curves indicate a sharp rise in $d\mu/dt$ when the temperature is sufficiently high for decomposition to take place.   H. M.

Temperature-coefficients of the Free Surface Energy of Liquids at Temperatures from −80° to 1650°. V. Measurements of Homologous Aromatic Hydrocarbons and Some of their Halogen Derivatives. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 405—415).—Data are given for benzene, toluene, p-xylene, mesitylene, ψ-cumene, cuminene, phenylmethane, chlorobenzene, bromobenzene, m-dichlorobenzene, p-bromofluorobenzene, m-fluorotoluene, and p-chlorotoluene. The hydrocarbons and their halogen derivatives afford examples of increase and decrease in the value of $d\mu/dt$ with rise of temperature. The deviations of the surface energy-temperature curves from straight lines are so large in many cases that they cannot possibly be accounted for by error of experiment. In the case of xylene, for instance, $d\mu/dt$ increases from 1·60 for the interval −19° to 3·0 for the interval 146° to 166°.   H. M.

Temperature-coefficients of the Free Surface Energy of Liquids at Temperatures from −80° to 1650°. VI. General Remarks. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 416—430). Compare preceding abstracts. From collected results recorded in the previous papers it would seem that the temperature-coefficient of the molecular surface energy may be independent of the temperature, or with rise of temperature may increase or diminish. No connexion can be traced between the class to which a particular liquid belongs and the magnitude of the molecular surface energy, or of its temperature-coefficient. The absence in general of a linear connexion between the surface energy and the temperature is supposed to be connected with the change of surface energy, and this departure from linearity is to be expected whenever the interval of temperature examined is large enough.

With regard to the connexion between the molecular surface

...gy and the chemical nature of the liquid, it is found that the ...ce energy at the same temperature increases in homologous ...es with the molecular weight. Replacement of hydrogen by ...gens, by the nitro- or amino-groups, and by aromatic hydro-...bon radicles leads to an increase in the molecular surface energy ...en the comparison is made at a fixed temperature. H. M. D.

The **Adsorption of Vapours.** A. M. WILLIAMS (*Trans. Faraday Soc.*, 1914, **10**, 167—171. Compare this vol., ii, 111).—... adsorption near to the saturated vapour pressure of a liquid ...ite and independent of the temperature, but is not necessarily ...aximum. C. H. D.

"**Negative**" **Adsorption.** A. M. WILLIAMS (*Trans. Faraday Soc.*, ..., **10**, 155—159. Compare this vol., ii, 111).—The adsorption of ...esium chloride and magnesium sulphate by charcoal increases ... the concentration to a maximum, decreases, passes through ...ro and becomes negative. Ammonium chloride also exhibits a ...aximum. C. H. D.

Action between Clay Filters and Certain Salt Solutions. B. HICKS (*J. Ind. Eng. Chem.*, 1914, **6**, 829—831).—Filtration ...ough porcelain clay filters produces little or no change in the ...neutral content of $N/10$-borate solutions, a slight decrease, about ... in concentration in $N/10$-alkali chloride and sulphate solu-...ns, a larger decrease in $N/10$-alkali carbonate solutions, and a ...ill larger decrease, 8%, in the case of $N/1000$ alkali carbonate ...tions. Ammonia and potassium are also absorbed by the filters ...m solutions of their salts; the retained ammonia may be removed ...washing the filter with potassium chloride solution, but in the ...se of potassium a small quantity is persistently retained by the ...ter even after persistent washing with water and ammonium ...loride solution. W. P. S.

The **Theory of Colloid Chemistry.** WILDER D. BANCROFT (*J. Physical Chem.*, 1914, **18**, 549—558).—A lecture delivered to the ...neral meeting of the American Chemical Society, in which a ...orking theory of colloid chemistry is discussed. The theory is ...sed on the four postulates: (1) Colloid chemistry differs from ...nary chemistry only through the variations resulting from the ...creasing dispersity of one or more phases. (2) Selective adsorp-...on occurs at surfaces. (3) Sufficiently finely divided particles, ...ich are prevented from coalescing, will be kept suspended in a ...dium by the Brownian movements; and (4) under fixed condi-...ons of peptonisation an approximately definite limiting concen-...tion is obtained corresponding with a saturated solution in the ...se of a true solution. J. F. S.

Equilibria in Ternary Systems. XVI. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 169—182. Compare ...is vol., ii, 634).—A further discussion of the equilibrium relation-

ships for the case in which one of the three components is practi-
cally non-volatile.   H. M. D.

New Form of Intermittent Siphon. W. A. BRADLEY
News, 1914, **110**, 163).—A simple form of intermittent ….
described, which permits of the automatic flushing of ….
in a gas absorption tube with a small quantity of ….
siphon is used in conjunction with a constant feed ….
the capacity of the flush can be varied by a simple …..
                                                                H. M. D.

Inorganic Chemistry.

Displacement of Acids by Hydrogen Peroxide
JOACHIM SPERBER (*Chem. Zentr.*, 1914, i, 2139; from *Schwei*. ….
Zeit., 1914, **52**, 245—248. Compare this vol., ii. 557 ….
of hydrogen peroxide on halogen acids has been further ….
The affinity of the halogen hydrides for hydrogen per….
the affinity of the halogen for oxygen, hydrogen iodide ….
decomposed. The reaction depends on the order in w….
substances are brought together. When hydrogen iodide ….
to hydrogen peroxide, the reaction is so violent that the ….
which is first liberated volatilises, leaving a colourless liquid ….
when hydrogen peroxide is added to an excess of the acid, ….
the reaction is vigorous, the iodine does not disappear. Exactly ….
reverse is the case with the other acids. The reaction ….
energetic when hydrogen peroxide is added to the acid. The ….
salts behave in the same way, from which it appears that h….
peroxide first liberates the free acid and then decomposes ….
view is supported by the fact that ammonium peroxide (D'Ans and
Wedig, A., 1913, ii, 1051) precipitates the peroxides from ….
of the alkaline earth haloids.   J. C. W.

The System Ammonia-Water. A. SMITS and S. Pos-
(*Proc. K. Akad. Wetensch. Amsterdam*, 1914, **17**, 182—194.—From
cooling-curve observations have enabled the authors to give a
complete description of the freezing-point diagram. The two com-
pounds $2NH_3,H_2O$ and NH_3,H_2O melt at $-78.9°$ and 79.6° respec-
tively. The eutectic point at which ammonia and $2NH_3.H_2O$ exist
as solid phases lies at 81.4 mols. % of ammonia and $-92.$ ….
point at which $2NH_3.H_2O$ and NH_3,H_2O co-exist lies at 55 ….
ammonia and $-86.0°$, and that corresponding with the co-exist-
of NH_3,H_2O and ice at 34.7% of ammonia and $-100.3°$. Except
the interval for mixtures containing 30—40 mols. % of ammonia
authors' data agree satisfactorily with those of Rupert (A., 1909,
726; 1910, ii, 605).

The vapour pressures of binary mixtures of varying composition have also been determined over a considerable interval of temperature, but the curves constructed on the basis of these data afford no trace of the formation of definite compounds.　　　H. M. D.

Action of the Silent Electric Discharge on Mixtures of Hydrogen and Nitrogen. M. LE BLANC (*Chem. Zentr.*, 1914, ii, 1, from *Ber. K. Sächs. Ges. Wiss., Math.-phys. Kl.*, 1914, **66**, _451.—Earlier experiments (Le Blanc and Davies, A., 1908, ii, 1; Davies, A., 1909, ii, 30) indicated that the formation of ammonia by the silent electric discharge does not obey the law of mass action. This might have been due to alterations in the electric conditions, caused by changes in the composition of the gaseous mixture. It is now found, however, that, even when the gases are largely diluted with a helium–neon mixture, the quantitative results are the same. The old experiments have been repeated with better apparatus, and the phenomena are found to be very marked. The amount of ammonia formed depends on the pressure of the apparatus, and the density and oscillation frequency of the current.　　　J. C. W.

Volatilisation of Arsenious Acid from Aqueous Solutions containing Hydrochloric Acid. BERTRAM JAMES SMART and WM T. PHILPOT (*J. Soc. Chem. Ind.*, 1914, **33**, 900—902).— Masses of 200 c.c. of hydrochloric acid solution of various concentrations both above and below that of the constant boiling mixture, and containing various quantities of arsenious acid, have been subjected to fractional distillation. The distillates have been analysed with the object of ascertaining to what extent and under what conditions the arsenic volatilises with the acid. It is shown that when solutions are distilled, those which contain the greatest concentration of hydrochloric acid give off the arsenic most rapidly. When hydrochloric acid is present to the extent of about 190 grams per litre or more, the concentration of arsenic in the solution as it is undistilled rapidly falls as the solution is fractionated. In solutions containing less than 180 grams of hydrochloric acid litre, the concentration of arsenic in the solution remaining undistilled rises, although some of the arsenic passes over, the ratio of hydrochloric acid and arsenic remaining practically constant until the solution contains about 185 grams of hydrochloric acid per litre. This point corresponds approximately with a hydrate of the formula HCl,H₂O. When the acid becomes more concentrated the proportion of arsenic volatilised increases rapidly.　　　J. F. S.

The Reduction of Arsenic Acid to Arsenious Acid by means of Thiosulphuric Acid. ROBERT M. CHAPIN (*Chem. Zentr.*, 1914, i, 2032—2033; from *J. Agric. Res.*, 1914, **1**, 515—517).— Arsenic acid is completely and quickly reduced to arsenious acid in cold by a mixture of sodium thiosulphate and a mineral acid. The speed of the reaction depends to a great extent on the concentration of the hydrogen ions, and the course of the reduction is

influenced by the amounts of the reagents and by the ⟨...⟩
which they are mixed. The reaction is therefore ⟨...⟩
appears to correspond with the reduction of a dichro⟨...⟩
sulphuric acid (compare Stiasny and Das, A., 1912, ii, ⟨...⟩

J. C. ⟨...⟩

Isotherm of the Solubility of Lithium Chloride at 25
Mixtures of Water and Ethyl Alcohol. S. PISA DE ⟨...⟩
(*Anal. Fis. Quim.*, 1914, **12**, 343—349).—The solubility of ⟨...⟩
chloride in aqueous alcohol decreases regularly in solvent ⟨...⟩
ing up to 70% by weight of alcohol; the solubility curve ⟨...⟩
linear, the coefficient being 0·6939 per gram of alcohol. The ⟨...⟩
during this stage exists as LiCl,H₂O. The anhydrous ⟨...⟩
posited from solutions in pure alcohol.   G. I⟨...⟩

Silicate Chemistry. II and III. **Lithium Alum⟨...⟩**
Silicates the Composition of which Corresponds with ⟨...⟩
of the Minerals Eucryptite and Spodumene. F. M. J⟨...⟩
and ANT. SIMEK (*Proc. K. Akad. Wetensch. Amsterdam*, i, ii, 2⟨...⟩
239—251, 251—270. Compare this vol., ii, 363). II. A ⟨...⟩
aluminium silicate of the composition LiAlSiO₄ has been prep⟨...⟩
from a mixture of lithium carbonate, alumina, and silica by h⟨...⟩
ing in a closed crucible at 1500°. When the fusion is slo⟨...⟩
cooled, small, irregularly shaped crystals are obtained, for ⟨...⟩
measurements of the mean refractive index and the density g⟨...⟩
$n_D = 1·531$ and $D = 2·362$ at 25°. These data indicate ⟨...⟩
artificial silicate is not identical with the mineral eucry⟨...⟩
the synthetic product has been named *pseudo-eucryptite.* ⟨...⟩
fusion is rapidly cooled by quenching, a pseudo-eucryptite ⟨...⟩
obtained, for which $n_D = 1·541$. This glass is metastable ⟨...⟩
gard to the birefringent crystalline modification, and is par⟨...⟩
converted into this on heating at 900°. The melting poi⟨...⟩
pseudo-eucryptite is given as 1388°.

The compound LiAl(SiO₃)₂ was prepared by fusion of a mi⟨...⟩
of the same substances containing a larger proportion of s⟨...⟩
The purest product obtained was found to melt at 1400°, with ⟨...⟩
$n_D = 1·521$ and $D = 2·411$ at 25°. Since the physical prop⟨...⟩
differ appreciably from those of the mineral spodumene ⟨...⟩
synthetic product has been named *β-spodumene.*

III. For the purpose of comparing the properties of ⟨...⟩
synthetic β-spodumene with the mineral varieties, the auth⟨...⟩
determined the melting points and densities of a numb⟨...⟩
kunzites and spodumenes. The data indicate that, in gene⟨...⟩
melting points of the natural kunzites are considerably high⟨...⟩
the values obtained for the synthetic products. It would s⟨...⟩
that the melting points of the minerals decrease as the dens⟨...⟩
increase.

Micrographic examination of the products which are form⟨...⟩
when the mineral varieties of lithium aluminium silicate are f⟨...⟩
and allowed to cool slowly afford evidence that β-spodumene ⟨...⟩
thereby formed. These observations lead to the conclusion ⟨...⟩

in natural kunzites, hiddenites, and spodumenes are metastable forms (a-spodumenes) of the compound, and that β-spodumene is the stable form at all temperatures below 1400°. The natural spodumenes cannot therefore be produced from dry magmas, and it is probable that their formation is due to so-called "hydrothermal" synthesis.

A lithium aluminate of the composition LiAlO₂ was prepared by fusion of a mixture of lithium carbonate and alumina at 900°, and then at 1200°. It forms microscopic hexagonal or octagonal plates which show pronounced double refraction. The indices were found to be $n_D = 1.604$ and $n'_D = 1.615$; $D^{20} 2.554$. The melting point could not be determined, but it is higher than 1625°.

<div align="right">H. M. D.</div>

Cæsium Alum and Its Properties. EDWARD HART and JESSE B. HUSELTON (*J. Amer. Chem. Soc.*, 1914, **36**, 2082—2084).—The solubilities of cæsium alum, expressed as the number of grams of the anhydrous salt, AlCs(SO₄)₂, per 100 grams of water, have been determined as follows: at 7°, 0.26; at 19°, 0.42; at 22°, 0.43; at 24°, 0.47; at 29.5°, 0.57; at 31.5°, 0.60; at 40°, 0.86; at 41°, .. at 47°, 1.17; at 49.25°, 1.39; at 50°, 1.42; at 56°, 1.86; at 62°, 2.06; at 66°, 2.85; at 68°, 3.13; at 80°, 5.78. Two determinations of the specific gravity of the hydrated alum gave a mean value 1.945. The crystals melt in their water of crystallisation at 117°. These values are compared with those recorded by other observers.

<div align="right">E. G.</div>

Influence of Certain Hydroxylic Compounds on the Solubility of Mercuric Chloride in Water. E. MOLES and M. MARQUINA (*Anal. Fis. Quim.*, 1914, **12**, 383—393).—Glycerol and glucose increase the solubility of mercuric chloride in water, whereas tartaric and citric acids decrease it. The solubility in glycerol is 1 in 1.25 at 25° ± 0.02.

<div align="right">G. D. L.</div>

Terbium. C. JAMES and D. W. BISSEL (*J. Amer. Chem. Soc.*, 1914, **36**, 2060—2066).—Urbain (A., 1909, ii. 671) has stated that terbium is homogeneous, whereas Welsbach (*Chem. Zeit.*, 1911, **35**, 658) has expressed the opinion that it consists of three different elements. The present paper gives an account of a further study of this question.

The material employed consisted of gadolinium oxide containing terbium oxide, together with dysprosium and holmium oxides and traces of yttrium and erbium. It was converted into the bromates, which were submitted to a long and careful fractionation. The results indicate that terbium is a single homogeneous element. The bromate process effects a comparatively rapid separation of terbium from gadolinium; neodymium, if present, comes between these metals.

<div align="right">E. G.</div>

The Acidic and Colloidal Characteristics of Aluminium Hydroxide. R. E. SLADE and W. G. POLACK (*Trans. Faraday Soc.*, 1914, **10**, 150—154).—Mahin, Ingraham and Stewart (A., 1913, ii,

139) stated that a solution of sodium aluminate is really a ɔɔ̣ːↄ
solution of the hydroxide in the alkali. It is now shown that ᵗʰᵉ
conclusions which these authors drew from their experiment̩ ᵃ
support of the above view, were unjustified. Conᵈᵘᶜᵗⁱᵛⁱᵗʸ
measurements of such solutions are against the assumṗṭᵢₒₙ ᵈ
colloidal particles, and, when hydrolysis takes place, cᵣʸₛₜₐ
aluminium hydroxide is deposited. The ultramicroscope ᵃᶠᶠᵒʳᵈˢ ₓ
conclusive evidence either way.   J. C. W.

Advances in the Metallurgy of Iron and Steel. Sₐ Rₒₐₙ
HADFIELD (*Trans. Faraday Soc.*, 1914, **10**, 1—43).—A ᵥ̣ₑ̣ₜₐ
delivered to the Faraday Society on June 11th, 1914. C. H. D.

Chromyl Chloride. II. E. MOLES and L. GÓMEZ (*Anal.* f₃
Quim., 1914, **12**, 142—154. Compare A., 1912, ii. 560). Aₙₐₗₑₛ
of recently prepared chromyl chloride give values very ᶜˡᵒˢᵉ ᵗ
the theoretical, and lead to the supposition that the earlier ᵃ ᵗʰᵉ
probably did not examine the pure compound. No chⱥⁿgₑ ᵢₛ
observed after two months, but after nineteen months ⱥ ⱨⱼ
coloured solid was deposited, which is possibly a polyᵐₑᵣᵢₛ

The heat of solution was found to be 17·86 cal. (Berthelot, 18:

The molecular weight, determined cryoscopically in carbon ᵗₑₜ
chloride, tin tetrabromide, and antimony pentachloride, ₚₒᵢₙₜₛ
the formation of molecular complexes in conformity with ᵗ
tendency to polymerisation noted above.   G. D. L.

Inorganic Solvents. I. Antimony Pentachloride
MOLES (*Anal. Fis. Quim.*, 1914, **12**, 314—343).—Pure antimon̩
pentachloride is lemon-yellow in colour, acquiring an orⱥⁿgₑ ᵗ
by the presence of chlorine. It has m. p. 3·0°, cryoscopic cₒₙₛₜ
18·5, heat of fusion 8·17 cal., and D₄° 2·3356.

The action of antimony pentachloride on potassium iodidₑ ₚᵣ
ably leads to the formation of iodine monochloride. Sₑₗₑₙᵢ
selenium, and tellurium yield the crystalline double compⱥⁿⱼs
their tetrachlorides with antimony pentachloride.   G. D. L.

Dilute Solutions of Aluminium in Gold. C. T. HₑYᶜₒₘₑ
F. H. NEVILLE (*Phil. Trans.*, 1914, [A], **214**, 267—276).—⸍
equilibrium relations exhibited by aluminium and gold have been
investigated by experiments on mixtures containing up to ⁵
weight of aluminium. The actual observations consisted ᵢₙ ᵗ
tracing of cooling curves and in the microscopic examination̩ ₒ
ingots which had been annealed at definite temperatures ⱥ
chilled by immersion in water.

The concentration-temperature diagram indicates the exⁱₛ
of two series of solid solutions (α and β), and of a compound
the composition Al_3Au_8. This compound is found in ⱥˡˡ
alloys containing from 18 to 28 atoms % of aluminium. Recⱥˡₑₛ
cence phenomena associated with the cooling curves of alloys ⁱ
taining from 10 to 27 atoms % of aluminium point also to
formation of a compound, $AlAu_4$. The relations between the si
phases are discussed with reference to an extensive series of miᶜ
photographs.   H. M. D.

Mineralogical Chemistry.

Mixed Carbonates from Traversella. MARIO DELGROSSO (*Atti Accad. Sci. Torino*, 1914, **49**, 1106—1117. Compare A., 1913, ii, 1).—The author has analysed a number of specimens from the Traversella deposits containing calcium, magnesium, and ferrous carbonates, together with small proportions of extraneous matter. The presence of ferrous carbonate is not always recognisable from the external characters, the most nearly colourless rhombohedral crystals often containing this carbonate in large proportions. In no one instance, where the conditions of deposition were evidently normal, was there any marked divergence from the relation $CO_2 = MgCO_3 + FeCO_3$. The conclusion is drawn that these minerals represent isomorphous mixtures of typical dolomite with real ankerite.   T. H. P.

Melilite and Other Minerals from Gunnison Co., Colorado. ESPER S. LARSEN and J. FRED HUNTER (*J. Washington Acad. Sci.*, 1914, 4, 473—479).—A complex of coarse-grained alkaline igneous rocks cuts near Cebolla and Beaver Creeks in the Uncompahgre Quadrangle, Colorado. One of these rocks, named uncompahgrite, is composed largely of melilite, together with pyroxene, perovskite, magnetite, and apatite. The melilite, occurring as large cleavage plates reaching a foot across, is colourless to grey with a greasy lustre, and closely resembles nephelite in appearance. It gelatinises only with weak acids; analysis gave I, D 2·98 (after deducting small amounts of apatite, calcite, magnetite, and perovskite). Two stages of alteration of the melilite are recognised: most frequently it is altered to a fine aggregate of garnet, diopside, idocrase, etc.; and at other times to the new mineral cebollite (see following abstract):

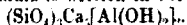|	TiO₂	Al₂O₃	Fe₂O₃	FeO	MnO	CaO
I. 43·73	—	10·80	—	2·04	0·16	34·63
II. 4·50	5·08	4·46	24·09	...	...	31·06

	MgO	Na₂O	K₂O	H₂O	Total
I.	4·35	3·40	trace	0·49	100·00
II.	0·52	—	—	—	99·51

Analysis II is of a black, titaniferous andradite from a soda-syenite allied to ijolite. A description is given of the perovskite present in these rocks, and also of anatase occurring as large, dark, translucent crystals on the joint planes of a diorite dyke.
      L. J. S.

Cebollite, a New Mineral. ESPER S. LARSEN and W. T. SCHALLER (*Washington Acad. Sci.*, 1914, 4, 480—482).—This mineral occurs as an alteration product of melilite at Beaver Creek, Gunnison Co., Colorado (see preceding abstract). It forms a dull, compact, white

to greenish fibrous aggregate; D 2·96, hardness 5. The
characters of the minute fibres suggest orthorhombic
The following analysis (after deducting 18·05% insolub
admixed diopside, garnet, idocrase, etc.) gives
$H_4Al_2Ca_5Si_5O_{16}$. Since the powdered mineral in water
alkaline with phenolphthalein, the group (CaOH) is
be absent, and the formula is written in the form:

$$(SiO_4)_3Ca_2[Al(OH)_2]_2.$$

The mineral gelatinises with acids, and is perhaps
zeolites.

SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	F$_2$O.	CaO.	MgO.	Na$_2$O.	K$_2$O.	
33·02	14·02	3·43	0·21	35·72	4·69	2·57	trace	

Analytical Chemistry.

Apparatus for the Analysis of Complex Gas Mixtures.
GUY B. TAYLOR (*J. Ind. Eng. Chem.*, 1914, **6**, 845—848).—In
apparatus described the Bone and Wheeler method of
tion (A., 1908, ii, 221) is combined with the usual
compensation burette, a copper oxide U-tube for the estimation
hydrogen and carbon monoxide, and a slow combustion burette
burning hydrocarbons. The absorption vessels dip into a
trough; the reagents are introduced by means of curved
under the lower edge of the absorption vessels, and after use
discharged by the aid of a suction apparatus. A trustworth
method for the separation of carbon monoxide, hydrogen, methane
and ethane is given.   W. P.

**New Method for the Precise Standardisation of Hydro-
chloric Acid Solutions.** LAUNCELOT W. ANDREWS (*J. Amer.
Soc.*, 1914, **36**, 2089—2091).—The following method for standard
solutions of hydrochloric acid depends on the loss of weight
by the conversion of silver nitrate into the chloride; its accur
is only limited by the errors of weighing.

Two similar silica or porcelain dishes, of 75—100 c.c.
are taken, each provided with a light cover and one of them
a stirring rod, short enough to lie under the cover. The
without a rod is referred to as the "companion dish." In the
other are placed about 2 grams of pure silver nitrate. Both
are put into an oven at 160°, and the temperature is raised
until the weight is constant. Fifty c.c. of 0·2N-hydrochloric
to be standardised are placed in each dish, the temperature of
solution when measured being noted. The silver nitrate is
up with the solution until it has dissolved and the silver chlor

Both dishes are heated at 95—100°, finally dried at cooled in the desiccator, and weighed. The increase in the weight of the companion dish represents the weight of non-volatile particles contained in the acid, and its amount is deducted from observed weight of the silver chloride. The normality of the solution is given by the expression $N = (H' - H'_1 + w_1 - w) / (0.026355 F)$, where F is the corrected volume of the solution, H' the weight of silver nitrate and dish, H'_1 the weight of the silver chloride, per nitrate, and dish, w the weight of the companion dish before experiment, and w_1 its weight at the close of the experiment.

E. G.

Estimation of Iodine in Connexion with Studies in Thyroid Activity E. C. KENDALL (*J. Biol. Chem.*, 1914, 19, 1—56. Compare A., 1912, ii, 864).—The author gives additional details and slight modifications of his process for estimating iodine in the presence of chlorides, bromides, and organic matter.

H. W. B.

Oxidation of Sulphur Compounds of Coal, and of Nitrogen in the Bomb Calorimeter, and the Correction to be applied in Estimating the Heat Value of Coal. SAMUEL H. FOSTER (*J. Ind. Eng. Chem.*, 1914, 6, 812—822).—When the chief sulphur compound of coal, pyrites, is burned with a non-gaseous fuel in the calorimeter in an atmosphere of oxygen under pressure, a fairly stable condition results. This condition is intermediate between the practically complete conversion to sulphur trioxide existing under the conditions of equilibrium at ordinary temperatures, and the almost total absence of sulphur trioxide characteristic of combustions without a catalyst to convert the sulphur dioxide into sulphur trioxide as the temperature falls. The relative amount of sulphur converted into sulphur trioxide increases with the amount of nitrogen oxides formed in the bomb. The nitrogen of coal is much more efficient in forming nitrogen oxides than is the nitrogen of the bomb gases; this, in connexion with the fact that in ordinary work the concentration of nitrogen in bomb gases before ignition is at least 5%, accounts for the more complete oxidation of the sulphur in coal to sulphur acid. Much too low results are obtained when coal containing pyrites equivalent to about 7% of sulphur is burned at 20 atmospheres pressure with 0.53% of nitrogen in the bomb gases. With higher percentages of nitrogen the results are more trustworthy. Usually, in burning coal with less than 2% of sulphur in a bomb calorimeter from which the air is not removed previously, there is sufficient formation of nitrogen oxides to ensure almost complete oxidation of the sulphur. The heating value of sulphur is found to be 4975 cal. per gram. W. P. S.

Chief Cause of the Loss of Sulphur Trioxide and of Chlorine by Incinerating Substances Containing these Constituents. JAMES O'SULLIVAN (*Analyst*, 1914, 39, 425—428).—During the incineration of substances containing chlorides the latter

are decomposed and chlorine is lost, but no reducti... ta... in the quantity of calcium, potassium, and sodium sulphate may be present. Magnesium sulphate undergoes deco... ignition unless a carbonate is present; in the absence of a ca... magnesium sulphate is converted entirely into magne... If present in sufficient quantity in a substance contai... magnesium sulphate may cause the whole of the chlorine t... when the substance is incinerated.   W P ...

Presence of Sulphates in Flour. R. A. C... and A ... WRIGHT (*Analyst*, 1914, **39**, 429).—The quantity of sulphate ... found in the ash of flour, amounting to about 0·02% of the w... of the ash, does not represent the amount of sulphates in the ... since, during ignition, the hydrogen phosphates present dec... the sulphates with loss of sulphuric acid. From 0·0069 to ... of sulphur trioxide is found if the flour is extracted with d... acetic acid and the sulphate precipitated in the solution by ... addition of barium chloride, after the proteins have been rem... by means of tannin solution.   W. P ...

Calcination of Magnesium Ammonium Phosphate ... **Causes of its Blackening.** JOSÉ GIRAL PEREIRA (*Anal. Fis...* ... 1914, **12**, 109—112).—The darkening of this phosphate on calc... tion is due in all cases to organic matter, which also deter... eventual formation of phosphides. In the absence of org... matter, the calcined substance remains quite colourless. G D L ...

Estimation of Carbon in Steel by the Direct Combustion ... **Method.** WM. BRADY (*J. Ind. Eng. Chem.*, 1914, **6**, 843—84... The method consists in the direct combustion of the met... oxygen; the carbon dioxide produced is absorbed in a ... excess of barium hydroxide solution. When the combustion ... completed, the barium carbonate and excess of barium hydr... are rinsed into a flask, and the hydroxide is titrated with stan... ised hydrochloric acid, using phenolphthalein as indicator. ... oxygen used is passed through potassium hydroxide solution an... soda-lime, and a tube containing granulated zinc is placed betwe... the combustion tube and the absorption apparatus to prevent an... sulphuric acid resulting from the oxidation of sulphur from pa... into the barium hydroxide solution.   W P ...

Estimation of Carbon in Steels and Irons by Direct Com... **bustion in Oxygen at High Temperature.** J. R. CAIN and H E ... CLEAVES (*J. Washington Acad. Sci.*, 1914, **4**, 393—397).—In ... ordinary method of estimating carbon in steels, etc., by comb... in oxygen, small additional quantities of carbon are obtained wh... the oxides are powdered and again heated in oxygen. The autho... in place of the latter procedure, increase the heat of the furnac... after the metal has been oxidised as far as possible under the us... conditions, and maintain the oxides in a state of fusion for abo... thirty minutes. In this way it was found that some steels ...

... more carbon and others give decidedly more, whilst with the increase amounts to nearly 0·02%. The barium carbonate ... method (this vol., ii, 577) was used for the estimation of carbon dioxide.

W. P. S.

Perchloric Method of Estimating Potassium, as Applied ... Water Analysis. CLARENCE SCHOLL (*J. Amer. Chem. Soc.*, 1914, ...—The method of estimating potassium as the perchlorate has been studied and proved to be accurate. Sulphates ... ammonium salts must be eliminated before applying the test, phosphates do not introduce any error, and therefore need not ... removed.

The method as modified for use in water analysis is as follows: ... measured quantity of the water is evaporated to 150 c.c., 10 c.c. ... concentrated hydrochloric acid are added, and the liquid is ... until it boils. Barium chloride solution (10%) is now intro... drop by drop until all the sulphates are precipitated, and ... boiling for fifteen minutes the solution is filtered, the filtrate ... rated to dryness, and the residue heated until all the ammon... salts have been expelled. The residue is dissolved in 20 c.c. ... water, a slight excess of 20% perchloric acid solution added, ... the solution evaporated to dryness. If white fumes do not ... the residue is redissolved in 10 c.c. of water, again treated ... perchloric acid, and evaporated to dryness; this process is ... until white fumes appear. The residue is now treated ... c.c. of 96—97% alcohol containing 0·2% of perchloric acid, ... up with a stirring rod, collected in a Gooch crucible, ... washed with the alcoholic solution of perchloric acid, ... at 120—130°, and weighed.

This method is rapid, simple, inexpensive, and accurate. E. G.

Estimation of Zinc in Treated Wood. M. HUME BEDFORD ... E. PFANSTIEL (*J. Ind. Eng. Chem.*, 1914, 6, 811). —The following ... recommended for the estimation of zinc in red oak which ... been treated with zinc chloride. Three grams of the sawdust, ... at 110° are mixed with 35 grams of sodium peroxide and ... in a bomb. The mass is then dissolved in water, the ... acidified with hydrochloric acid, boiled, and 2 grams of ... acid, 10 c.c. of concentrated nitric acid, and 5 c.c. of 8% ... chloride solution are added. The mixture is rendered alkaline, ... excess of concentrated ammonia are added, and, after dilu... to 100 c.c., the zinc is titrated at 80° with standardised ... potassium ferrocyanide solution.

W. P. S.

Detection of Lead in Toxicology, Particularly in Urine in ... of Lead Poisoning. G. MEILLÈRE (*J. Pharm. Chim.*, 1914, ... 10, 225—231).—Small quantities of lead in solution may be ... by adding copper sulphate to the solution, precipitating ... metals with hydrogen sulphide, dissolving the mixed sulphides ... acid, and then separating the lead from the copper electro... In the case of urine, the quantity voided during twenty-... hours is treated with 1% of its volume of hydrochloric acid,

1 gram of copper sulphate is added, and the mixture is treated
with hydrogen sulphide. The precipitate is collected on a filter,
washed, then dissolved in nitric acid, the solution evaporated, and
the residue heated until the copper nitrate is converted into the
oxide. This residue is dissolved in 6 c.c. of nitric acid, the whole
is diluted to 100 c.c., and submitted to electrolysis. Small platinum
electrodes are employed; the whole of the lead is deposited as an
anode within twenty-four hours by using a current at 2 volts and
of such amperage that there is but a slight evolution of gas at
the anode. The deposit of lead peroxide may be weighed, and is
identified by dissolving it in nitric acid containing oxalic acid and
applying suitable tests to the solution.   W. P.

Method of Estimating Small Quantities of Lead in
Solder, etc. PIERRE BRETEAU and PAUL FLEURY (*J. Pharm. Chim.*,
1914, [vii], **10**, 265—273. Compare this vol., ii, 77-. The alloy
is fused with a mixture of sodium carbonate and sulphur, the
mass is treated with boiling water, and the lead, copper, and tin
sulphides are collected on a filter. These sulphides are then dis-
solved in hydrochloric acid containing bromine, the solution
treated with sulphurous acid to reduce the iron, and, after a few
minutes, potassium cyanide and potassium hydroxide are added,
the addition of sodium sulphide to the alkaline solution causes
lead to be precipitated as its sulphide, whilst the iron and tin
remain in solution. The lead sulphide is collected, dissolved in
dilute nitric acid, the solution evaporated, and the residue dried
for one hour at 150°. The residue is then dissolved in water, the
solution again evaporated, and heated. The lead nitrate so
obtained is dissolved in 5 c.c. of water, a small crystal of sodium
acetate is added, and the solution is poured slowly into a known
excess of standard potassium dichromate solution; the dichromate
solution must not be added to the lead solution. The lead chromate
is then collected on a filter, washed with water, and the excess
dichromate is estimated in the filtrate. The potassium dichromate
solution may conveniently contain 0·1432 gram of the salt per
5 c.c. of this solution are equivalent to 0·001 gram of lead. The
copper and iron may be estimated by the usual methods in the
filtrate from the lead sulphide after the hydrogen sulphide
has been expelled by boiling the solution with the added
sulphurous acid.   W. P.

Separation of Vanadium and Phosphorus with "Cupferron."
VICENTE GARCÍA RODEJA (*Anal. Fís. Quim.*, 1914, **12**, 378-382).—
After reduction of the vanadate to the hypovanadate, the vanadium
is quantitatively precipitated by freshly prepared cupferron
solution, and the phosphate may be estimated in the filtrate.
                                                          G. B.

An Arrangement for the Detection of Residual Acetylene
Hydrocarbons in Caoutchouc. L. LUTZ (*Chem. Zentr.*, 1914,
102; from *Bull. Sci. Pharmacol*, 1914, **21**, 193—195).—An
arrangement of a flask fitted with a delivery tube, bent into

ght angles, is described, in which finely cut caoutchouc may be ... with water so that, while the water is condensed in the first ... tube, any volatile hydrocarbons pass over into a suitable ...

J. C. W.

Hydrogen Number of Some Essential Oils and Essential Oil Products. I. Oils of Sassafras, Anise, Fennel, Clove, and Pimento. ALAN R. ALBRIGHT (*J. Amer. Chem. Soc.*, 1914, **36**, ...)—Fokin (A., 1908, ii, 637) has suggested the determination of hydrogen numbers for unsaturated compounds corresponding with the iodine numbers of Hübl and Wys. It has now been found that a hydrogen number can be assigned to certain ... oils, colloidal palladium being used as the catalyst. Some ... especially those with a constituent containing an allyl or propenyl group, are capable of very rapid hydrogenation. Such compounds are so rapidly reduced that, in the case of an oil containing one of them, the allyl or propenyl groups are quantitatively ... before other configurations are attacked to more than ... extent. The hydrogen number of the oil is defined as the ... of c.c. of hydrogen at 0° and 760 mm. which are absorbed ... gram of the oil during the period of most rapid absorption of gas.

In order to determine the hydrogen numbers of the oils of ..., anise, fennel, clove, and pimento, experiments were first ... with the active constituents of the oils, namely, safrole, ... and eugenol. Imitation oils were then prepared containing the particular active constituent in the proportion in which it ... in the natural oil, the remainder being represented by ... As limonene itself absorbs hydrogen fairly rapidly, the ... afforded a somewhat severe test of the hydrogenation ... determination. Samples of commercial oils were subsequently submitted to the hydrogenation process. The hydrogen ... of the various substances and oils are recorded.

E. G.

New Reaction for Resorcinol. PARIDE TORTI (*Boll. Chim.*, 1914, **53**, 265).—When a little resorcinol is heated with a few ... of nitric acid (D 1·40), an intense red coloration is formed. ... reaction is visible with as little as 0·00025 gram of resorcinol, ... forty times as sensitive as the reaction with ferric chloride. ... cool, the liquid deposits minute, reddish-brown, acicular ... which are soft to the touch, and dissolve in water, ... ether, or chloroform.

T. H. P.

Estimation of Sugar in Blood. PHILIP A. SHAFFER (*J. Biol.*, ... 1914, **19**, 285—295).—A method is described for estimating ... sucrose in 5 c.c. of blood. Its essential features consist in ... the proteins by combined heat coagulation and the ... Rona colloidal iron precipitation, and, after heating with ... solution, estimating the cuprous oxide formed, by ... permanganate method or by simply dissolving the oxide ... acid, treating with ammonia, and comparing with a

standard ammoniated copper solution in a colorimeter. When
the processes, including the reduction, are carried out in certain
tubes, and the precipitates collected and washed by centrifuga-
tion.

The method previously described, involving the use of
alcohol for the precipitation of the proteins in the blood, gives
lower results for the blood sugar, and is therefore regarded as
unsatisfactory.   H. W. B.

**Estimation of Aldoses. I. The Action of Neutral Sodium
Hypoiodite.** N. BLAND and L. L. LLOYD (*J. Soc. Chem. Ind.*,
1914, **33**, 948 949).—In the examination of the action of a dilute
on sodium hypoiodite, it was found that the reaction with for-
aldehyde proceeds quantitatively according to the equation
$NaIO + CH_2O = NaI + H \cdot CO_2H$, and may be used for the estimation
of the aldehyde in aqueous solution.   Five c.c. of a commercial
formalin are diluted to 1 litre, and 10 c.c. of this solution are
added to 50 c.c. of $N/10$-iodine solution, previously rendered
slightly alkaline with sodium hydroxide. After five minutes the
mixture is acidified with sulphuric acid, and the liberated iodine
is titrated with thiosulphate solution. Untrustworthy results are
obtained when the method is applied to paraformaldehyde or
acetaldehyde.

In the case of sugars, neutral sodium hypoiodite oxidises
the aldehyde group; for instance, the aldehyde group in dextrose
requires one molecule of iodine or hypoiodite.   Lævulose and
sucrose contain no aldehyde group, and do not react with neutral
hypoiodite, but the latter sugar, on inversion, yields dextrose and
lævulose, and requires one molecule of iodine.   The following
results were obtained with different sugars; in each case 10 c.c.
of a 1% solution of the sugar were added to a mixture of 10 c.c.
of $N/10$-iodine solution and 50 c.c. of $N/10$ sodium hydroxide
solution (this produces a neutral solution); after five minutes'
contact, the solution was acidified, and the liberated iodine titrated.
Dextrose, 96·4 to 99·7%; lactose, 99·1 to 99·4%; maltose, 99·1 to
101·8%; sucrose (after inversion), 100·8 to 101·3%; lactose (after
inversion), 99·1 to 99·4%; maltose (after inversion), 99·1 to 99·4%.
                                                               W. P. S.

Estimation of Pentosans. J. VAN HAARST and S. C. J. OLIVIER
(*Chem. Weekblad*, 1914. **11**, 918—925).—A comparison of results
obtained in the estimation of pentosans by Tollens's method and
that given in the Dutch "Codex Alimentarius." The authors
commend distilling with hydrochloric acid at the standard rate
400 c.c. in two hours. A slower rate tends to decompose part of
the furfuraldehyde, while more rapid distillation fails to effect
complete decomposition of pentosans containing arabinose. The
results obtained by Tollens's method are more accurate than those
given by the process of the "Codex Alimentarius," but none of
the published tables for calculating the amount of the pentosans
gives the velocity of distillation employed in their compilation.
                                                               A. J. W.

Estimation of Hydrogen Cyanide in Feeding Stuffs, and Occurrence in Millet and Guinea Corn. J. R. FURLONG (*Analyst*, 1914, **39**, 430—432).—The method consists essentially in conversion of the hydrogen cyanide into Prussian blue, and estimation of the latter colorimetrically. One hundred grams the ground substance are extracted for three hours in a Soxhlet apparatus with 90% alcohol. The extract is transferred to a flask, and after the alcohol has been distilled off, 150 c.c. of 10% sulphuric acid are added, and the distillation is continued, the distillate being collected in a receiver containing 5 c.c. of 10% potassium hydroxide solution. After one hour the receiver is emptied, water is added to the flask, and a second quantity of distillate collected. These operations are repeated until the evolution of hydrocyanic acid ceases. The distillate is concentrated to ... c.c., boiled for ten minutes with the addition of 1 c.c. of 20% iron sulphate solution containing 1% of ferric chloride, cooled, treated with hydrochloric acid, and 10 c.c. of glycerol are added. After about fifteen hours, the mixture is diluted with water to ... c.c., and the blue coloration compared with that given by known quantities of hydrogen cyanide under similar conditions. When the amount of hydrogen cyanide present is not less than 0·001 ... the standards may be made up directly, but with smaller quantities it is necessary to dilute to 150 c.c. and then concentrate, in the preparation of the solution from the substance under examination. Estimations of hydrogen cyanide in millet and guinea corn plants of various ages showed that all the young ... contained a cyanogenetic glucoside, whilst the full-grown ... were free from this substance. In the case of guinea corn, yield of hydrogen cyanide reached a maximum (0·01%) in the ... plants, and decreased as growth proceeded. With millet ... maximum amount (0·045%) was found in the plants which attained a height of 24 inches.   W. P. S.

Cause of Acidity of Fresh Milk of Cows and a Method for Determination of Acidity. LUCIUS L. VAN SLYKE and ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1914, **19**, 73—76).—The ... of fresh milk is due to the presence of acid phosphates. ... of alkali to milk leads to the hydrolysis of the calcium present, so that by the direct titration of milk with alkali, ... phenolphthalein as indicator, results are obtained for the ... which may be twice as great as they should be. The ... must, therefore, be removed before titrating with the ... by treating 100 c.c. of milk with 2 c.c. of a saturated ... of normal potassium oxalate, and keeping the mixture for ... than two minutes.   H. W. B.

Sulphocarbon Oil. F. CANZONERI and G. BIANCHINI (*Ann. Chim. anal.*, 1914, **2**, 1—9).—The authors describe the composition, properties, and means of detection in mixtures of the so-called "sulphocarbon" oil. that is, olive oil extracted by means of carbon ... sulphide.   T. H. P.

Specific Reaction of Oils of Marine Animals and the Products of Hydrogenation. M. TORTELLI and E. JAFFÉ (*Chim. Applicata.* 1914. **2**, 80—98).—The reactions pr-viously described as specific for the oils and fats of marine animals are due to impurities or to products of alteration which may be eliminated by the purification, and may also be found in fats and oils of industrial or vegetable origin. The authors find, however, that the following test is given by the oils and fats of marine animals and by no others; the quantities in brackets represent the proportion to be taken in examining a fat obtained by catalytic hydrogenation. Into a graduated cylinder of about 15 mm. in diameter and 15 c.c. (25 c.c.) in capacity, and fitted with a ground stopper, are introduced 1 c.c. (5 c.c.) of the oil or melted fat, 5 c.c. (10 c.c.) of chloroform, and 1 c.c. (1 c.c.) of glacial acetic acid, which are shaken to give a homogeneous mixture. With this 40 drops (2·5 c.c.) of a 10% solution of bromine in chloroform are vigorously agitated for a few seconds, the cylinder being then placed on a sheet of paper. If the oil is derived from a marine animal, the liquid becomes first red and, within a minute, green, the colour increasing in intensity for some time and then remaining constant for an hour. The coloration is formed more rapidly with highly refined oils, and varies from green with a yellowish reflection to green with a bluish reflection, according to the origin of the oil. In the case of a hydrogenated oil, the first coloration is reddish-yellow, and the final intense green colour is obtained with greater rapidity than with the non-hydrogenated oils.

The reaction serves for the detection of the presence in alimentary fats of synthetic fats prepared from the oils of marine animals.   T. H. P.

Drying Urine for Chemical Analysis. WISFRED W. LOMB (*J. Biol. Chem.,* 1914, **19**, 105—113).—In drying urine of herbivora for the determination of the heat of combustion, it is found that large quantities of ammonia and carbon dioxide are evolved. The methods used to remove the water are (1) to use a desiccator over sulphuric acid at about 5 mm. pressure and low temperature, and (2) to pass over the sample a current of air free from ammonia and carbon dioxide. The loss of nitrogen under these conditions may amount to as much as 50% of the nitrogen of the urine, and arises mainly from the decomposition of ammonium carbonate, and not of urea or hippuric acid. The carbon dioxide is lost in a quantity more than sufficient to combine with the ammonia lost to form the normal carbonate.

The author estimates the total carbon and total hydrogen (excluding that of the water) in the fresh undried urine by combustion in an ordinary combustion furnace; this method gives consistent results.   H. W. B.

A Permanent Preparation of Urease, and its Use in the Estimation of Urea. DONALD D. VAN SLYKE and GLENN E. CULLEN (*J. Biol. Chem.,* 1914, **19**, 211—228).—Urease in powder form
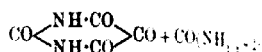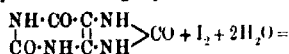
ared by **extracting soja bean** meal with water at room tem-
perature, and **then pouring the clear** extract into at least ten times
its volume of **acetone.** The precipitated urease can be dried in
vacuum, and **maintains** its activity for an apparently indefinite
period. It is soluble in water, and the solution, if kept at 0°, does
lose its activity for several weeks, especially if 5% of dipotassium
hydrogen phosphate is also present in the solution.

For estimating urea in urine, one-half c.c. of urine is mixed with
1 c.c. of 0.6% potassium dihydrogen phosphate and 1 c.c. of a 10%
solution of urease. After twenty minutes at 15°, or three minutes
only, to complete the decomposition of the urea, 4 to 5 grams of
potassium carbonate are added, and the ammonia then aspirated
into 25 c.c. of $N/50$-hydrochloric or sulphuric acid. When the
action is finished, the excess of acid is titrated with $N/50$-alkali.
Urease is a particularly valuable reagent because it enables a
direct estimation of the urea in the blood to be made, its action
being so specific that no other constituent of the blood is attacked.
The original paper must be consulted for the details of the methods
and apparatus recommended by the authors.   H. W. B.

Estimation of Uric Acid in Urine. DOMENICO GANASSINI (*Boll.
Chim. Farm.*, 1914, **53**, 257–262).– In the author's method the
following solutions are employed : (1) Salkowski-Ludwig reagent,
prepared by mixing equal volumes of (*a*) and (*b*) immediately
before using : (*a*) 26 grams of silver nitrate are dissolved in
500 c.c. of distilled water, and ammonia solution added until
the brown precipitate at first formed dissolves completely, the
whole being then made up to 1 litre with water ; (*b*) 100 grams of
magnesium chloride and 150 grams of ammonium chloride are dis-
solved in about 500 c.c. of distilled water, ammonia solution in
excess added, and the volume made up to 1 litre. (2) Aqueous 2%
uranyl acetate prepared in the hot ; this serves as a defecating and
precipitating agent, mucinoid substances and uranyl phosphate being
precipitated, together with pigmentary matter. (3) Decinormal
alkali solution containing 25 grams of potassium iodide per litre.
A 0.1% aqueous solution of indigo-carmine. The procedure is
as follows :

One hundred c.c. of the urine are mixed with 20 c.c. of the
uranyl acetate solution, and the liquid at once poured on to a dry
folded filter. Sixty c.c. of the filtrate are introduced into a 100 c.c.
beaker containing 10 c.c. of the Salkowski-Ludwig reagent, the
mixture being well stirred, and, after a short time, the precipitate
collected quantitatively on a small filter, and washed three or four
times with water. Most of the precipitate is then returned to the
precipitation vessel by means of a glass rod, and treated with about
60 c.c. of a solution of 2 grams of potassium iodide in 150 c.c. of
water. The turbid liquid thus obtained is then poured through the
filter containing the remainder of the precipitate, which is washed
several times with the potassium iodide solution. The filtrate,
consisting of about 150 c.c. of colourless, almost clear liquid, is
acidified by the addition of a drop or two of acetic acid, and

rendered alkaline by means of about 5 grams of [.......] ....
The solution is then made slightly but distinctly [.......] ....
more drops of the indigo-carmine solution, and is [.......] ....
shaken with decinormal iodine solution until a single ....
immediate change from blue to yellowish-green. The ....
c.c. of decinormal iodine used, multiplied by 0.0[..] ....
amount of uric acid in grams per 100 c.c. of the urine. ....
accuracy of the method has been tested by means of both ....
solution of pure potassium urate and urines containing ....
added proportions of uric acid.

The action of iodine on uric acid in presence of borax is [.......]
by the following equation :

$$\begin{array}{c} NH\cdot CO\cdot C\cdot NH \\ | \quad \quad || \\ CO\cdot NH\cdot C\cdot NH \end{array}>CO + I_2 + 2H_2O =$$

$$CO<\begin{array}{c} NH\cdot CO \\ NH\cdot CO \end{array}>CO + CO\cdot NH_{[..]}$$

The alloxan thus formed is also acted on by the iodine [...]
action is so slow as to be virtually negligible; the same is true
with the purine derivatives, other than uric acid, occurring [....]

T H P

**Separate Estimations of the Purine Substances and
Uric Acid in Urine.** DOMENICO GANASSINI (*Boll. Chim. [..]*
1914, **53**, 262—265).—This method is based on the fact that
silver-magnesium precipitate yielded by the Salkowski-L[...]
reagent is, when thoroughly washed and suspended in [...]
neutral towards phenolphthalein. When, however, highly [...]
trated aqueous potassium iodide is added, the precipitate [....]
almost completely, and the liquid becomes intensely alkaline ....
to the formation of normal potassium urate and of the p[...]
salts of the other purine derivatives present. The alkalinity ...
liquid is, therefore, directly proportional to the content [....]
compounds, inclusive of the uric acid. The latter may al[..] ...
be estimated separately in the same liquid by the method [...]
described (preceding abstract).

The procedure is at first similar to that used in the estimati[..]
uric acid alone (*loc. cit.*), with the exception that the preci[..]
given by the Salkowski-Ludwig reagent is washed with dist.
water until the washing water fails to react alkaline with [...]
phthalein or litmus. The solution of this precipitate in the [...]
ium iodide solution, amounting to about 150 c.c., is titrated [..]
$N/20$-sulphuric acid solution in presence of 5—6 drops of [..] [..]
holic phenolphthalein. Four or five grams of potassium hyd[..]
carbonate and 10 drops of 0.1% indigo-carmine solution are [..]
added to the liquid, which is titrated with $N/10$-iodine s[..]
until the blue colour changes to green. Multiplication of the [..]
of the number of c.c. of $N/20$-sulphuric acid over that of
$N/10$-iodine by 0.0076 yields the number of grams of purine [..]
pounds, calculated as xanthine, in 50 c.c. of the urine. The [...]

[c.c. of] $N/10$-iodine, multiplied by 0·0084, gives the grams of [acid] in 50 c.c. of the urine.　　　　　　　　T. H. P.

Some New Tests for Veronal. H. Lucas (*Pharm. J.*, 1914, [42]).—The odour of iodoform is observed when veronal is [heated] with aqueous sodium hydroxide, and the resulting solution [cooled] and then warmed with a solution of iodine.

The residue obtained by fusing veronal with sodium hydroxide [gives] a purplish-violet biuret reaction with a drop of aqueous [copper] sulphate, and liberates nitrogen (not quantitatively) by [treatment] with concentrated sodium hypobromite.　　　C. S.

Estimation of Antipyrine. W. O. EMERY and S. PALKIN (*J. Ind. [Eng.] Chem.*, 1914, **6**, 751—753).—The method depends on the solu[bility] of iodoantipyrine in chloroform. In the case of antipyrine [pure] or in such admixture that after treatment with iodine no [substance] other than iodoantipyrine will be extracted by chloro[form, a] quantity of the sample containing not more than 0·25 gram [antipy]rine is shaken with 20 c.c. of water, 5 c.c. of alcohol-free [chloro]form, 0·5 gram of sodium hydrogen carbonate, and a slight [exce]ss of iodine solution. After a short time, the excess of iodine [is destroy]ed by the addition of a few drops of thiosulphate solu[tion, the] iodoantipyrine is shaken out with chloroform, the chloro[form] solution is washed with water, filtered, evaporated in a [tared] flask, and the residue is weighed. The weight of the resi[due] multiplied by 0·5992 gives the quantity of antipyrine present. [When] the antipyrine is mixed with phenacetin, sulphonal, or [other] substance, a weighed portion of the sample is shaken with [c.c.] of water, 20 c.c. of concentrated hydrochloric acid, and an [exce]ss of iodine solution. After some hours the liquid is decanted [through] a glass-wool filter, the tarry residue is washed with 5% [hydro]chloric acid, then dissolved in about 50 c.c. of methyl alcohol [(which] must be free from ethyl alcohol and acetone), the solution is [dilut]ed with 50 c.c. of water and sodium hydrogen carbonate, and, [after] the excess of iodine has been destroyed by the addition of [thio]sulphate solution, the iodoantipyrine is extracted with chloro[form].　　　　　　　　　　　　　　　　　W. P. S.

[Use] of Manganese Carbonate in the Detection of Traces [of] Strychnine. G. GUÉRIN (*J. Pharm. Chim.*, 1914, [vii], **9**, [435]).—The author finds that the sensitiveness of the test for [strychn]ine by means of sulphuric acid and potassium dichromate [is exag]gerated, and that the detection of 0·01 mg. by this method [is un]certain. This quantity can be readily detected by the re[agents] of Mandelin (0·5 gram ammonium vanadate in 100 grams [of pure] sulphuric acid), of Wenzell (potassium permanganate [0·2 gram] in pure sulphuric acid [100 grams]), or of Sonnenschein [(solu]tion of the alkaloid in pure sulphuric acid and addition of a [litt]le of cerium oxide). According to the author, the last two [reage]nts appear to be more sensitive than that first named.

[A] method which is as sensitive as any of those described above [consi]sts in dissolving the alkaloid in two or three drops of sulphuric

acid and adding 2—3 mg. of manganese carbonate. On ....
blue coloration is developed, which gradually becomes .....
then pink.

**Application of Tungsten Salts to the Analysis of Tanning
Materials.** ALEXANDER T. HOUGH (*J. Soc. Chem. Ind.*, 1914,
847—848).—Two reagents, prepared from sodium tungstate, ...
ently give different results (amounts of precipitate) with the ...
tannin, and it is suggested that it may be possible to estimate .
purity of a given tannin extract by the constancy of the ...
between the two results. The reagents are prepared as : ....
(1) 10% sodium tungstate solution, 5 c.c.; water, ...
ammonium chloride solution, 3 c.c.; (2) 10% sodium .....
solution, 5 c.c.; 8% hydrochloric acid, 2 c.c.; 25% ammon.
chloride solution, 3 c.c. A tannin solution is made .....
about 4 grams of tannin per 250 c.c., and 10 c.c. of this ....
are mixed with 10 c.c. of the first reagent; the mixture .....
on a filter, and 10 c.c. of the filtrate are evaporated to dry
and the residue is weighed (*A*). The precipitate on the ...
then dissolved in hot water, the solution is added to the rem...
of the filtrate, and the whole is evaporated to dryness *B* ...
actual weight of the precipitate is $B - A$; it is necessary to ..
tain the weight of the precipitate by this indirect meth.. ..
cannot be washed. A similar estimation is then made, ...
second reagent. The amount of precipitate is calculated
percentage of tanning material in the extract, and for ....
pose the quantity of total solids and of tannin (*C*) in 100 .
the extract is estimated. Then $100(B - A)/C$ gives the ....
number " of the tannin, using the first reagent; the same ...
gives the "tungstic number," using the second reagent, ...
sumably, "tungstic"/"tungstate" $= K$ for any given ....
material. The author has applied the method only to .....
extract, in which case $K = 1·0503$.   W. P. ...

**Quantitative Estimation of Aspartic and Glutamic Ac
in the Products of Protein Hydrolysis.** FREDERICK WILL
FORRMAN (*Biochem. J.*, 1914, 8, 463—480).—After bri..
of the protein with hydrochloric acid, the glutamic and as..
acids are converted into their calcium salts, which are then ..
tatively precipitated by the addition of alcohol. After ...
from the alcohol-soluble calcium salts of the other ....
present, the free acids are regenerated by dissolving in wat...
adding oxalic acid. Traces of accompanying impurities are .
removed by successive treatment with silver sulphate and ...
tungstic acid. The resulting solution on evaporation ye...
crystalline mass, which is now extracted with glacial ace...
The residue consists of a mixture of glutamic and aspart..
and the proportionate quantity of each present is calculated .
the carbon content of the mixture. As the difference betwe..
percentages of carbon in glutamic and aspartic acids is as gre..
4·73, the proportion can be determined with tolerable accura..

A small quantity of the glutamic acid is transformed into pyrrolidonecarboxylic acid during the preliminary processes indicated above, and is found in the glacial acetic acid extract. It is estimated by measuring the amino-nitrogen before and after boiling with hydrochloric acid, which reconverts the ring compound into glutamic acid.

The actual separation of aspartic and glutamic acids is effected by fractional crystallisation of the copper salts, copper aspartate crystallising out first. When most of the aspartate has been removed, the larger portion of the glutamic acid is separated by converting it into the hydrochloride.

By means of this method, caseinogen is found to contain 21·77% glutamic acid and 1·71% of aspartic acid, or about twice as much as has hitherto been accepted.　　　　　　　　　　H. W. B.

The Ferric Alum Estimation of Casein.　H. V. Arny and H. Schaefer (J. Ind. Eng. Chem., 1914, 6, 748—751).—Two alterations have been made in a method described previously (1906, ii, 407) for the estimation of casein in milk; to ensure of filtration, the mixture of milk and ferric alum solution is made for one hour before the precipitate is collected, and the titration is made with $N/50$-thiosulphate solution. The method, as used at present, is as follows. Five grams of milk are met with 5 c.c. of ferric alum solution (48·2224 grams of $NH_4(SO_4)_2,12H_2O$ per litre), and, after one hour, the precipitate collected on a filter and washed until free from soluble iron. The filtrate is treated with 3 c.c. of 31% hydrochloric acid and grams of potassium iodide, heated to 40° for thirty minutes in a closed flask, and the liberated iodine is titrated with $N/50$-sulphate solution. Each c.c. of the ferric alum solution required for the precipitation is equivalent to 0·05934 gram of casein.
　　　　　　　　　　　　　　　　　　　　　W. P. S.

Comparison of Methods for the Determination of the Proteolytic Activity of Pancreas Preparations.　J. H. Long and A. W. Barton (J. Amer. Chem. Soc., 1914, 36, 2151—2166).— The object of this work was to compare the different standards for valuation of the various commercial trypsins or pancreatins. The proteolytic value of six such trypsin preparations has been compared by four distinct methods, namely, the metacasein reaction, the Fuld-Gross sodium caseinate digestion method, the formaldehyde titration of amino-acids produced by digestion, and the fibrin digestion. The results obtained by the four methods agree in arranging the activities of the six preparations in the same order, but they do not agree as to relative quantitative value of the different ferments, for the strongest ferment according to the metacasein reaction appears to be about twelve times as strong as the weakest, and according to the fibrin digestion about ten times as strong, whilst by the other tests the relation obtained is as 4 or 3:1. Still greater irregularities appear in comparing some of the other preparations.

The products sold as trypsins or pancreatins probably contain at least two different enzymes, reacting in different ways on proteins, and the effects produced in any case depend on the proportions in which the enzymes are present. These enzymes possess different degrees of stability towards heat.

It is not at present possible to convert the proteolytic value of tryptic ferment from the terms of one standard to those of another, since the products are made by very different processes, which probably yield mixtures of ferments in widely different proportions, together with unknown quantities of inorganic salts. A more rational definition of trypsin is desirable, and products should be made to conform to interchangeable standards.
                                                                            E. G.

Electrical Method of Estimating Salt in Soil. WILLIAM BEAM and GILBERT A. FRKAK (*Cairo Sci. J.*, 1914, **8**, 130—). In estimating the amount of soluble salts in soils by the electrical conductivity method, the error due to the nature of the salts present may be corrected by constructing special tables for the particular combination of salts in the area under examination. The result is especially affected by sodium carbonate, and the resistance is higher when much organic matter is present (Davies and Bryan, U.S. Dept. Agric. Bur. Soils, Bull. 61). A more important error is that due to the presence of calcium salts (especially sulphate), which is not only harmless, but beneficial in neutralising the effects of toxic salts. This error is avoided by extracting the salts with 40% alcohol instead of water, and comparing the results with those obtained with a solution of salt in the same solvent; the calcium sulphate may then be estimated, if desired, by extraction with water as well.

In the case of soils containing moderate amounts of salts, the method usually employed is to treat an amount of soil, containing about 20 grams of dry matter, with 100 c.c. of 40% alcohol, and shake for ten to fifteen minutes. Shaking for one minute gives nearly the same results, and variations, from 38—42%, in the strength of the alcohol are without much influence.

In testing the method with solutions of known concentration, a solution containing 0·030% of gypsum and 0·131% of sodium chloride was found to have a resistance of 210 ohms instead of the calculated resistance of 220 ohms.   N. H. J. M.

Estimation of the Lime Requirement of Soils by means of [Barium Hydroxide]. C. R. MOULTON and P. F. TROW-BRIDGE (*J. Ind. Eng. Chem.*, 1914, **6**, 835—837).—The lime requirement of a soil, as estimated by boiling the soil with an excess of N/10-barium hydroxide solution and measuring the excess by means of the ammonia set free from added ammonium chloride, is proportional to the quantity of barium hydroxide used, and is due to the acidity of the soil. The result obtained is considerably less than when the Vietch method is employed. Further, the lime requirement varies with the duration of the distillation and the volume of the distillate until the lime requirement falls to nil (compare Bizzell and Lyon, this vol., ii, 150).   W. P. S.